*Office of the Quartermaster General*
*Military Planning Division*
*Research and Development Branch*

# FLAMEPROOFING TEXTILE FABRICS

*Prepared by a Staff of Specialists*
*under the Editorship of*

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*under Research Project Q.M.C. #27*
*of the National Research Council*
*National Academy of Sciences*

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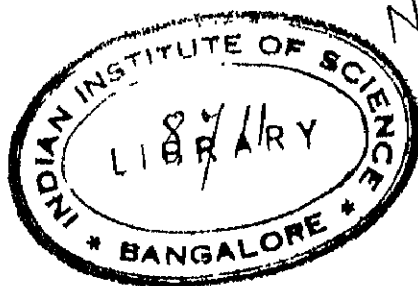
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# General Introduction

American Chemical Society Series of
Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A.C.S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this introduction) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first monograph of the series appeared in 1921. After twenty-three years of experience certain modifications of general policy are indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. This differentiation is fast becoming nebulous. Research in private enterprise has grown apace and not a little of it is pursued on the frontiers of knowledge. Furthermore, most workers in the sciences are coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and

now frankly recognize that their objectives are common, namely search for new knowledge for the service of man. The officers of Society therefore have combined the two editorial Boards in a sin Board of twelve representative members.

Also in the beginning of the series, it seemed expedient to consti rather broadly the definition of a monograph. Needs of workers had be recognized. Consequently among the first one hundred monogra appeared works of the form of treatises covering in some instances rath broad areas. Because such necessary works do not now want for pu lishers, it is considered advisable to hew more strictly to the line of t monograph character which means more complete and critical treatm of relatively restricted areas, and where a broader field needs covera to subdivide it into logical sub-areas. The prodigious expansion of n knowledge makes such a change expedient.

These monographs are intended to serve two principal purposes: fir to make available to chemists a thorough treatment of a selected area form usable by persons working in more or less unrelated fields to the e that they may correlate their own work with a larger area of physic science discipline; second, to stimulate further research in the speci field treated. To implement this purpose the authors of monographs a expected to give extended references to the literature. Where the lite ature is of such volume that a complete bibliography is impracticabl the authors are expected to append a list of references critically select on the basis of their relative importance and significance.

# Foreword

The pressing demands of war have always served as a stimulus to research and development in the field of Science. The recent conflict, coming as it did at the time of our entrance into what has been termed the "Age of Science," imposed particularly heavy demands upon the technical ability of our scientists to discover and develop new instruments of warfare and corresponding protective devices.

Our early experiments focused attention upon the desirability of developing suitable methods for rendering military fabrics resistant to flame propagation. A preliminary survey of existing flame-retardant treatments indicated the need for basic research on the general subject of flameproofing. Research has been defined as: "studious inquiry; usually, critical and exhaustive investigation or experimentation having for its aim the revision of accepted conclusions, in the light of newly discovered facts." In nearly every instance the problems facing the Armed Services were approached along the avenues of research in the firm belief that herein lay the quickest and most satisfactory solution. Certainly, in the search for suitable methods of flameproofing cotton fabrics intended for military usage, a thorough understanding of the fundamental mechanisms involved has led to a wholesome revision of previous concepts and a clearer recognition of the potentialities of available processes. In addition to meeting specific military needs, the researches conducted represent the first extensive study of the fundamentals of flameproofing and have laid a firm foundation upon which future investigations may be based. The success of the research programs undertaken is attributable to the cooperation and perseverance of those actively engaged therein, both in civilian and military capacities.

In agreement with the proposition of Thomas Hobbes, that "the main purpose of science is the tying of facts into bundles," it was felt that the experiments performed and the findings thereof should be collected and presented to the interested public With that in mind, this monograph on "Flameproofing Textile Fabrics" was prepared

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# Preface

The need for practical methods of combating fabric inflammability was brought forcibly to the attention of many branches of the Armed Services upon our entry into World War II. Programs were initiated in many service laboratories with the intention of investigating the practical application of flameproofing treatments to various military fabrics.

Initially, Quartermaster Corps activities in the field of flameproofing were concentrated upon the application of flame-retardant finishes to tentage duck. At the same time, similar programs dealing with the flameproofing of fabrics were in progress in other service laboratories. The Army Corps of Engineers at the Engineer Board, Fort Belvoir, Virginia, was engaged in the development of commercial as well as field impregnation methods for the treatment of camouflage netting. The Navy at the Industrial Test Laboratory, Naval Shipyard, Philadelphia, Pennsylvania, pursued a similar investigation of the flameproofing of life jackets. The Chemical Warfare Service Development Laboratories at the Massachusetts Institute of Technology, Cambridge, Massachusetts, investigated suitable methods for the flameproofing of summer flying suits for Air Corps personnel. During the North African campaign it became apparent that fire-resistant finishes should be available for general use on clothing fabrics.

In view of the fundamental nature of the research which it was evident would be required to attain a satisfactory solution of this problem, the Research and Development Branch, Military Planning Division, Office of the Quartermaster General, requested the National Academy of Sciences to initiate a research program. Accordingly, in October, 1943, the National Research Council of the Academy contracted with Columbia University for the establishment of a research project in the Department of Chemical Engineering on the subject "The Flameproofing of Army Clothing."

The results of these researches, conducted over a period of a little less than three years, are being made available to the general public in this volume. In addition, the report includes a great deal of related information on the general subject of flameproofing which was obtained through other Quartermaster Corps programs and research projects in other service laboratories.

It is believed that making this information generally available will stimulate further research in the field, particularly that of a more fundamental nature. Furthermore, it will greatly advance the knowledge of

other investigators working along the same lines. In this way, it should possible to obtain, within a relatively short time, even better flame-r tardant finishes for military fabrics than are known today as a result wartime researches.

It was felt particularly desirable to publish this volume at this time order that the results of the various investigations might be recorded so after completion of the experimental programs and to avoid any po sibility that the information would not be disseminated in a consolidat form. Furthermore, recent legislation pertaining to the fire hazard textiles now under consideration in various state legislatures as well as Congress emphasizes the importance of making this material available a matter of public safety.

The subject matter of this book has been presented as a comprehensi survey of the subject of flameproofing textile fabrics rather than in t form of a technical report of the investigations carried out. The materi has accordingly been divided into three general sections which consider turn the fundamental mechanisms of the thermal degradation of cellulo and the chemical or physical phenomena of flameproofing; the metho employed in the processing and evaluation of flameproofed fabrics; a the various applications which exist for flame-retarding treatments in t field of textile fabrics. This type of presentation should enable the read to become familiar with the types of retardants available, the function these agents in the prevention of flaming and glowing, and the methods which they are applied and evaluated before attempting to appreciate t differences in performance when applied to fabrics.

Chapter I serves as an introduction to the subject of flameproofing. attempt has been made to clearly define the objectives of flameproofi treatments, the requirements which might be set up for an ideal treatme and the variables influencing the effectiveness of a flameproofing agent. glossary of terms has also been included with the intention that the co fusion which currently exists in the nomenclature employed in discussio of flameproofing would be avoided, at least in the interpretation of t subject matter of this volume.

In Chapter II, the nature of cellulose is reviewed briefly followed by thorough discussion of its normal degradation reactions. It was thoug that this background was necessary in order to attack the more compl problem of high temperature degradation. The reader is then introduc to the thermal degradations of cellulose at elevated temperatures and t nature of the decomposition products obtained. The influence of flam retardant materials upon the formation of these products is proposed one of the primary effects of flameproofing.

The fundamental causes of the prevention of both afterflaming a afterglow are considered in Chapter III. In this case the mechanis which have been commonly proposed in the literature on the subject a

presented along with more recent theories which possess a firmer foundation in experimental fact.

The purpose of Chapter IV is to thoroughly acquaint the reader with the test methods commonly employed in the evaluation of flameproofed fabrics. In some cases, the tests described are specific for fabrics intended for military purposes and would not be widely applicable in the textile industry. Many of the tests included, however, have been developed or improved in the course of war research projects and may warrant a more widespread usage.

Chapter V is intended to present a survey of the general types of treatments available, the variables which exist in the application of these agents to the fabric, and the industrial processing techniques employed in commercial practice. The value of this section has been enhanced by the inclusion of adequate experimental data to illustrate the effects of the variables discussed.

In Chapter VI, the relative efficiencies of many of the better available treatments are compared in regard to their suitability for use in the processing of military uniforms. The criteria employed include not only laboratory evaluation techniques but also practical wearing tests.

A similar comparison of flameproofing treatments and their applicability for use on military fabrics other than articles of clothing is made in Chapter VII. Included in this group is a consideration of flameproofed tentage fabrics which probably represent the principal application of flame-retarding treatments in the textile industry to date.

The final chapter on civilian applications (Chapter VIII) points to the need for an effective and durable flameproofing treatment. In addition, current restrictions and proposed legislation are discussed along with the question of implied warranty.

The book includes as many of the different flameproofing treatments and as much of the available data as could conveniently be considered. An attempt has been made to group the flameproofing agents according to the manner of their performance and select the data which would best illustrate the points discussed.

Though the publication of information of this type in the form of a collaborative volume possesses many obvious disadvantages, the scope of the subject matter as originally envisioned and the time allotted for completion made it highly impractical for any one person to write the book in its entirety. Furthermore, since the experimental work described was carried out in several different government and industrial laboratories, having one of the individuals closely connected with the original investigation contribute the write-up of the experiments performed helps to insure that valid conclusions are drawn on the data obtained and serves as an acknowledgment of the contributions of the individual or organization.

The selection of authors was generally made on the basis of those best

qualified and at the same time best able to submit their contributic within the allotted time. In many cases the task was difficult since ma of the individuals considered were already overburdened with the respo sibilities of their regular positions. The response to the invitations w gratifying, however, and those who refused were prompted to do so by t pressure of previous commitments.

Since the majority of the work described was performed under gover ment contracts and many of the contributors were in the employ of varic government agencies, it was felt to be improper to allow royalties to acc to the authors. Instead, all royalties have been applied to a reduction the purchase price of the book. This is wholly in accord with the origi objective of making the subject matter available to the greatest number interested persons.

The editor wishes to express his sincere appreciation to the seve authors. In every instance they cooperated to the full extent of th ability despite other heavy demands upon their time. In addition, I a deeply indebted to the members of the editorial board who were mutua charged with the organization of the subject matter and selection authors as well as the editing and compiling of the manuscript itse Without the cooperative effort of this group the task would have been but impossible.

Special appreciation is due Miss Charlotte Yater whose familiarity w the subject matter considered rendered her particularly suited to the ta of preparing and compiling manuscripts and also assisting in the readi of proof.

The preparation of the subject index was carried out by Miss Cyntl Berlow.

Graphs and illustrations in the text were prepared by Prof. Frank Lee of Columbia University.

Grateful acknowledgments are extended to the many others who ha contributed to the preparation of this book in any way and to the individuals to whom we are all indebted for carrying out the actual labo tory investigations. Special mention should be made of Dr. Milton Har Dr. M. W. Sandholzer, and Mr. K. S. Campbell who contributed adv and criticism on the contents of some sections.

Further acknowledgments are also due to many individuals in the I search and Development Branch of the Office of the Quartermaster Ge eral and to the National Research Council Committee on Quartermas Problems of the National Academy of Sciences for their interest a cooperation.

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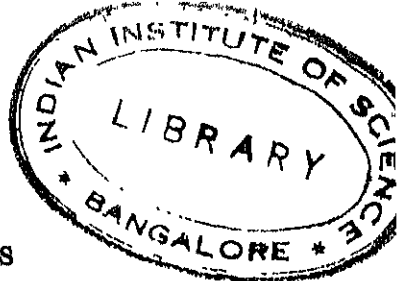

## Section One

# FUNDAMENTALS

# Chapter I

## Flameproofing Defined

*James M. Church*

**Development of Flameproofing.** Ever since the beginning of man, he has been actively engaged in seeking improvements in his existence both from a personal standpoint as well as in the interest of the welfare of others. Included in man's pursuit of happiness down through the ages has been his persistent search for some means of combating fire, which has destroyed some of his most priceless possessions and at times has left him destitute, causing loss of life, home and property. During the advance of the civilization of man we note his progress in this respect, mainly through methods of control. The first attempts were confined to the development and use of materials which would withstand the action of fire and have finally culminated in the construction of our present-day fireproof buildings and structures. Of the many fire-resistant materials discovered and perfected by man, none have been found suitable for protection in the form of clothing. The natural fibers which have been used for ages, spun and woven together into fabrics, are all combustible to varying degrees, but otherwise possess those characteristics of warmth, wear, flexibility and beauty which are paramount for clothing purposes. With the advent of man-made fibers, it has been the aim of the scientist to perfect the ideal fiber which also includes the desired fire-resistant qualities. In some respects this has been accomplished to the extent of developing synthetic fabrics of much greater resistance to fire than some of those made from natural fibers.

The recent world war with its holocaust of destruction by fires originating from incendiaries, flame throwers and the use of highly combustible fuels brought about a greater renewed effort by the scientists to find better means of protection against fires which cause ignition of the clothing and result in burn casualties. The modern type of warfare with its mechanized armored machines brought with it new dangers to the military personnel, which in the early days of the war resulted in high loss of life and disabilities.

The results of scientific researches carried out during war times for the protection of military personnel inevitably find ready uses in the peacetime civilian life to follow. This will undoubtedly be true in the case of

flameproofing. Local, state and federal legislation in the interest of pul safety are already demanding greater fire protection from the use clothing and interior fabrics, in order to avoid the calamities which reported almost daily in the press due to injuries sustained from fi originating from combustible fabrics. In this modern scientific age mar now prepared to offer some definite solution to this perplexing problem, incorporating with the fibers chemicals which will greatly retard th combustibility and thus prevent ignition of the fabric.

**What Is Flameproofing?** The term "flameproofing" would imply t employment of some method to prevent the ignition of a combustil material, thus restricting its destruction by flame. However, througho the literature on this subject, there is still considerable confusion betwe such terms as "fireproofing," "flameproofing," "flame-resistant," "no glowing," etc., even to the extent of using some of these interchangeabl Since there exist degrees of combustibility of materials, it would see best to define these in a general way to limit the degree of combusti within a specified range. When describing a material as "fireproofed," tl use of this term should convey the meaning of total resistance to destru tion by fire and should not be used with any of the lower fire-resista types of materials. Likewise in the case of a material which does not witl stand the action of fire without some change in its physical state, but do prevent self-combustion once the igniting source has been removed, tl term "flameproofed" would be applicable in its description. The less fire-resistant materials which do not burn too readily may likewise l characterized as "flame-resistant."

One characteristic of cellulosic materials different from most combu tibles is their tendency to be consumed, after the flame has been extir guished, by a glowing, non-flaming type of combustion. This raises th question in characterizing the inflammability of combustible types c cotton goods whether one should not differentiate between flaming an the glowing tendencies during combustion of the fabric. In the case o certain flameproofing treatments which have been applied to the fabric i order to reduce its susceptibility to combustion, it is possible to render th cloth fairly flame-resistant and yet it will be consumed by an aftergloy which persists even after the source of the heat or flame has been removed In some respects this afterglow may prove to be of more serious conse quence than the flaming usually associated with fires. The heat resultin from afterglow is in most cases more intensive than the flame, resulting ir serious damage and injury, besides the possibility that it might produc renewed flaming. Therefore in the use of the term "flameproofing" as ap plied to fabrics, it should imply not only resistance to continued flaming but also include the absence of any afterglow. In other words, both non-flaming and non-glowing should be included in the term "flameproofing" when used to characterize any cellulosic or other material capable of

being consumed by a glowing type of combustion. For a practical use of this term, in evaluating such materials, it is desirable to define the amount of afterflaming and afterglow, rather than attempt to make its use limited to those materials which exhibit absolutely no tendency toward either, since in most instances a slight amount is evident but does not persist for any appreciable time.

Furthermore, in carrying out flame test measurements of fabric combustibility, the recognition of a slight afterflame or afterglow is often dependent upon the person performing the test. A flame or glow of a fraction of a second's duration is often confused with optical after-images or with the light emanating from the incandescent carbon filaments during the brief cooling period. The latter phenomenon should not be confused with the progressive, exothermic oxidation of the char.

For these reasons a fabric is regarded as flameproofed if it shows no afterflaming of a measurable amount, and no afterglow in excess of four seconds after the flame has ceased. To differentiate between fabrics which may be resistant to one but not to the other, the terms "flame-resistant" and "glow-resistant" may be applied individually, but should be further characterized by denoting, in terms of seconds' duration, the degree of resistance offered in both respects.

**Classification of Flame Retardants.** Since flameproofing agents are chemical substances it is only natural that any attempt at a classification would include a grouping according to similarities in their chemical structure. This would permit listing various types of phosphates, sulfates, borates, sulfamates, salts of zinc, antimony, tin, or other similar compounds together for a convenient chemical classification. This, however, is found to be of little use from a practical standpoint since various compounds of the same type behave entirely differently as fire retardants. This is brought out forcibly in the comparison of the various phosphates, which in the case of the weaker basic salts are efficient flameproofing agents but with the stronger basic salts such as tri-sodium phosphate or the more insoluble metallic phosphates the latter are very ineffective

From the preceding discussion of the terms to be applied in characterizing the degree of flameproofing to be obtained by the use of various retardants, one might be inclined to group the flameproofing agents into classes according to whether they exhibit complete flame and glow-retarding tendencies, or perhaps only a partial flame and glow resistance. Such a classification leads to confusion in borderline cases of retardants which under some circumstances may be effective flameproofing agents when employed in certain combinations, but which under less favorable circumstances offer only a weak resisting action toward the combustion of the fabric by flame or glow. Unless a close distinction is permitted in the requirements set up for the various classes, it would be likewise rather difficult to determine whether a given retardant is of the "flameproofing" or

the "flame-resistant" type, in such borderline cases. Therefore any c sification based upon the performance of a flame-retardant chemical n be restricted to a general grouping and as such becomes useful in cl acterizing the various agents according to whether they possess good fla proofing or glowproofing qualities or whether they are of the milder t of flame-resistant or glow-resistant agents.

One of the most useful classifications for a practical flameproofing textile fabrics is one which is not based on their relative effectiveness, rather upon their durability in offering continued resistance to the infl mability of the fabric during its use. Any worthwhile commercial tre ment would require not only an initially effective flameproofing but which would be capable of some resistance toward any action tending remove it or destroy its effectiveness. Such a classification would per listing the different flameproofing agents or treatments as either (1) te porary, (2) semi-durable, or (3) permanent. The first class would incl the water-soluble retardants, which for the most part are highly effici but are readily removed by a simple immersion in water, thus destroy their effectiveness. The second class, on the other hand, would incl those capable of withstanding the action of a water leach but which easily removed or destroyed by stronger solutions of salt or soap as countered in sea water immersion or laundering operations. The last a more durable type are those agents which will resist the action of stronger leaching solutions within a reasonable degree and therefore, w certain precautions as to the severity of the treatment, can be depend upon to offer continued protection to the fabric in preventing compl combustion by flame. Standard leaching tests are now available for eval ation of the various flameproofing agents according to their permanen as defined above. This is accomplished by merely limiting the type leaching solution for the three classes to (1) ordinary tap water, (2) lute salt and mild neutral soap solutions, and (3) common commerc soap solutions as employed in commercial laundering practice. The exa conditions of each leaching test can be readily defined in terms of te perature and duration of leach required before effectiveness of the flam proofing is impaired.

Further considerations of a suitable classification of flame retardan might well include some specification of requirements based upon the e fectiveness obtained from a given amount of the chemical, or the rever in terms of the quantity of retardant necessary to produce a given degr of flameproofness. The latter is perhaps the most convenient standard adopt since it offers a suitable comparison of the relative effectiveness the various agents on a weight or per cent add-on basis. Minimum requir ments for effective flameproofing agents can therefore be established terms of the add-on required to produce a minimum afterflaming, afte glow and resulting char area as measured by the standard flame tests.

Formerly, the flame test requirements for treated fabrics in general al lowed for a short two-second afterflaming and a maximum char length o 3.5 inches but no measurement of afterglow was made. More recent de velopments, particularly in the adaptation of flameproofing treatments tc clothing fabrics, where the performance requirements might well be morc severe, have necessitated raising the flame test specifications.

In the case of the Vertical-Bunsen burner flame test the standard requirements for acceptable treatments have now been established as (1) no afterflaming, (2) less than 4 seconds' afterglow, and (3) less than 3.5 inches of char length. In adhering to this specification in adopting the 45°-Microburner flame test as the preferred standard, the requirements on a comparative basis would be much the same, namely, (1) no afterflaming, (2) less than 4 seconds' afterglow, and (3) less than 2.5 square inches of char area. The quantity of retardant required for the treatment of a fabric to meet the above flame test specifications might then be considered as the "minimum effective add-on" and could be used for comparative purposes in the evaluation of flameproofing agents.

**Other Factors Affecting Flameproofing Efficiency.** In addition to the effectiveness of the fire retardant as discussed in the foregoing section, there are several other factors which greatly affect the efficiency of the flameproofing treatment. The first of these is the type and structure of the fabric to be treated. The majority of the considerations of this volume have been confined to the flameproofing of cellulose fabrics. This type of fabric constitutes the great majority of the textile fabrics either in the form of cotton goods or the regenerative type of rayon Furthermore, cellulose is one of the more combustible types of fiber and would therefore warrant more serious considerations of possible methods of flameproofing than perhaps most of the other fibers However, this does not preclude the possibility that many of the treatments discussed here are equally applicable to fabrics woven from other natural or synthetic fibers Since, however, the mechanisms governing flameproofing phenomena are concerned chiefly with chemical reactions involving pyrolysis and combustion, it is logical to conclude that changes in the chemical structure of the fiber might well radically alter either the rate or direction of the reaction and result in less effective flameproofing with a given retardant or treatment. For this reason the processing of other types of fabrics for an efficient flameproofing may present an entirely different problem which may or may not require a different method of approach for solution.

In similar fashion, variations in the weight and weave of the fabric introduce corresponding variables in application of effective flameproofing agents. In the case of cotton goods, these factors concern themselves mainly with the amount of retardant required and the conditions for application for an effective flameproofing treatment. This conclusion is based upon the fact that the components of cellulose and fire retardant are com-

mon to all types of cotton fabric, and if intimate contact of the two is obtained in the treatment, the underlying requirements of the flameproofing mechanisms are satisfied.

Another of the factors affecting the degree of flameproofness obtained from a given fire retardant is inferred in the above discussion. This is concerned with the conditions employed in the treatment of the fabric with the flameproofing agent. From a consideration of the mechanisms evolved for explaining flameproofing phenomena it would follow that the main object of any treatment should be to achieve a uniform and intimate distribution of the retardant within the fabric in close contact with the individual fibers. This is evident from the fact that the water-soluble agents afford a maximum degree of flameproofing with a minimum amount of retardant. Here the highly dispersed solution of the agent permits a complete and thorough distribution of the chemical within the fabric structure. In the case of the less soluble retardants, the large particle sizes very definitely limit the possibility of uniform and intimate distribution, and this is accountable, at least in part, for the fact that much greater amounts of these agents are required to obtain an equally effective treatment. Therefore thoughtful consideration should be given in the application of any chosen flameproofing agent to a given fabric which will include a selection of the best conditions and methods possible for the treatment in order to achieve this ultimate object. In many instances the only approach, with due regard to the physical properties of the flameproofing compound, is one of a systematic investigation of the variables to be encountered in the treatment or method by trial and error type of experimentation.

Most of the treatments and field tests reported here were made with an 8.5-oz. olive drab herringbone twill which constitutes a high percentage of military uniforms in the form of combat and fatigue suits and coveralls. In investigating the effects of the added ingredients of dye, sizing and extraneous matter occurring in the finished cloth it was found that these were mainly of a minor consequence in the effectiveness of the flameproofing agents, provided the treatment allowed for an intimate and uniform distribution of the agent. Actually in testing grey goods, dyed goods and sized fabrics, these ingredients were found to contribute slightly to the flameproofing qualities of the treated fabric. In other words, the natural pectin, wax or resin present in the original fabric, or the added dye and resin employed in the finishing of the fabric are in reality flameproofing agents of a low order. These substances, however, interfere in some instances with the effectiveness of the treatment by rendering the fabric less acceptable to the flameproofing agent. This is particularly true in the case of sizing components which in most cases should be removed by a preliminary desizing treatment prior to the flameproofing treatment in order to prepare the fabric in a more absorptive state. After the flame-

proofing treatment the sizing may be restored for effecting a finish to the cloth but should be applied in such a way as not to disturb the distribution of the flameproofing agent.

In many regards the 8.5-oz. desized herringbone twill offers an excellent type of cotton fabric for adoption as the standard for evaluation of flameproofing treatments. Its texture and weight may be considered as typical and representative of the majority of cotton fabrics for consumer use. It is therefore suggested that this type of cotton cloth be adopted as the standard testing fabric for all flameproofing specifications in evaluation tests.

**Ideal Characteristics of Flameproofing.** The most desirable flameproofing agent would be one which could be easily applied to a fabric, preferably in a finished form ready for use, and would render that fabric permanently flameproofed without appreciably altering the fabric characteristics for consumers' use. This definition of an ideal flameproofing agent might at first glance not appear too unreasonable but further analysis would show it to be highly idealistic in view of present-day facts concerning flameproofing. And yet it serves its purpose in presenting an ultimate specification for flameproofing, which will challenge those attempting improvements toward a more satisfactory solution of this problem. It is not wholly improbable that such a flameproofing agent may some day be discovered, for science does not recognize any situation as being impossible regardless of its difficulties. Only by means of a thorough understanding of the problem in all of its aspects will scientists of the future achieve this coveted goal, and it is to this purpose that the following discussion of the fullest meaning of these ideal specifications is dedicated.

Ease of application has been the one requirement, in addition to a high degree of effectiveness, that has made the water-soluble agents so popular, even though they are readily removed by the slightest leaching action and are apt to produce a deleterious effect to weaken the fabric strength. In terms of permanency, the better of the agents are the most difficult to apply, which would make it appear that ease of application and permanency do not go hand in hand The requirement of durability includes many factors and is not confined to launderability alone although this factor has been of major importance. Permanency against the conditions of aging and storage and against the action of salt spray or salt water is sometimes more difficult to attain with certain agents than protection against laundering. Excessive humidity and temperature, as encountered in tendering tests, may tend to destroy the flameproofing treatment, as well as impair the strength of the fabric through the decomposing action of the agent. In the application of the more permanent types of flameproofing agents, it has been found necessary to employ an excessive amount of the retardant in order to obtain an effective treatment. In doing so, not only is the weight of the fabric increased appreciably but

usually the hand is greatly impaired. As might also be expected in such cases, excessive amounts of the treatment may affect the permeability of the fabric. In this regard both air and vapor transmission are important, otherwise clothing fabrics are certain to produce discomfort to the wearer by causing excessive heat loads for lack of proper heat transmission. In most cases of clothing fabrics, nontoxicity of the chemical retardant is a necessary prerequisite. Not only must the treatment not contain harmful chemicals but the treatment itself must not induce any harshness to the fabric finish which might cause a rash or dermatitis condition upon the skin of the wearer. Since textile fabrics for consumer use require other treatments and finishes, any acceptable flameproofing treatment must be compatible with the others. In the matter of efficient flameproofing from the use of chemical retardants, only those which will limit the inflammability of the fabric to the extent of no afterflaming and a minimum of afterglow can be regarded as of major importance. An added requirement might also include that the char resulting from the limited combustion of the fabric be of a substantial type which will contribute some protection against further exposure to the flame source. Such chars have been shown to offer a considerable degree of insulation.

In summary, the following requirements should be considered in the selection of any flameproofing agent or treatment:

1. A minimum effective add-on to avoid both an excessive increase in the weight of the fabric and the imparting of a poor hand to the fabric.

2. Means of easy application to the fabric, which may permit its use directly with garments or consumer goods.

3. A reasonable permanency of the treatment toward the leaching action of water, salt and soap solutions, and dry-cleaning solvents.

4. Freedom from any deleterious action upon storage or during conditions of use which may cause a decrease in the fabric strength through a tendering action.

5. No appreciable decrease in the permeability of the fabric as measured by both air and vapor transmission.

6. Compatibility of the treatment with other treatments used in the finishing of the fabric.

7. Avoidance of any physiological action of the retardant on the skin, both in the treatment and wear of the fabric.

8. A flameproofing efficiency which prohibits the propagation of any flame and any appreciable afterglow, resulting in a charred fabric which still retains considerable of its strength characteristics.

**Glossary of Flameproofing Definitions.** The following general terms, to be encountered throughout this volume, are listed here with their definitions for a ready reference and a better understanding of the full meaning of flameproofing as discussed in the following chapters of this book.

*Add-on*—Weight increase of fabric due to absorbed flameproofing agent or solution after treatment. Usually applied to the dry weight basis, otherwise termed "pickup."

*Afterflame*—The time in seconds which the fabric flames after the source of flame has been extinguished.

*Afterglow*—The time in seconds which the fabric glows after all flaming has ceased.

*Char Area*—The blackened area resulting after all flaming and glowing have ceased. Usually well defined and easily measurable by use of a planimeter.

*Char Length*—Used only in the Vertical flame tests and represents the furthest distance of the damage caused by flaming or glowing as measured from the originating point of the flame or lower edge of the fabric strip.

*Combustion*—Chemical decomposition caused by a combination of the substances with oxygen causing evolution of light and heat in a burning reaction.

*Fabric Weight*—Expressed in ounces per square yard.

*Fill*—Threads of the weave of a fabric which are at right angles to the selvage.

*Flame Retardant*—A material which imparts resistance to afterflame to the fabric.

*Flame Test*—Standard procedures employing different types of flame for testing the flameproofness of a fabric.

*Flameproofed Fabric*—A treated fabric which exhibits appreciable resistance to both afterflame and afterglow in the standard flame tests

*Flameproofing Agent*—A material which imparts resistance to both afterflame and afterglow to the fabric.

*Flame-resistant Fabric*—A fabric treated as to inhibit afterflaming in the standard flame tests.

*Glow-resistant Fabric*—A fabric treated as to inhibit afterglow in the standard flame tests.

*Glow Retardant*—A material which imparts resistance to afterglow to the fabric.

*Heat Load*—Excessive accumulation of body heat. Usually measured by increase in sweat rate, pulse, and body temperature.

*Herringbone Twill*—A weave characterized by diagonal lines produced in a ribbon effect by a series of floats or skipped threads staggered in the direction of the warp.

*Minimum Flameproofing Requirements*—A treatment which provides afterflame, less than 4 seconds' afterglow, and char length or char ar of less than 3.5 inches or 2.5 square inches respectively by the Vertic Bunsen burner and the 45°-Microburner tests.

*Pickup*—Weight increase of a fabric following treatment. Usually en ployed for a wet weight increase.

*Pyrolysis*—Chemical degradation caused by the action of heat. May accompanied by combustion if carried out in the presence of air.

*Sizing*—Any added material which imparts body to a yarn or fabr

*Tendering Action*—Any effect of the chemical agents used in the trea ment of a fabric, or conditions of exposure of the fabric which will resu in loss of fabric strength.

*Warp*—Threads of the weave of a fabric which are parallel to the selva edge.

# Chapter II

# Degradation of Cellulose

Prior to considering the reactions occurring in the flaming of cellulosic materials or the mechanisms by which that combustion may be prevented, it is desirable to review briefly the chemical nature of cellulose and its behavior under normal conditions.

It should be borne in mind that in considering the flameproofing of cotton textiles one is dealing with the chemical treatment of a very complex polymeric material. In order to properly interpret the behavior of flame-retardant materials and also the performance of flameproofed fabrics it is essential that one consider carefully the known reactions of cellulose under the influence of acids, bases and oxidizing materials. A clear understanding of the causes and mechanisms of the hydrolytic and oxidative degradations of cellulose will contribute considerably to an understanding of the changes observed in the course of thermal degradation Furthermore, the performance of treated fabrics in the course of normal use and storage under various environmental conditions can be interpreted only on the basis of the known reactions of the cellulose molecule.

Accordingly, the following sections have as their purpose a thorough presentation of the basic structure, fundamental properties and known reactions of cellulose.

## A. NATURE OF CELLULOSE

*Henry A. Rutherford*

### 1. Occurrence and Structure of Cellulose

Of all the organic compounds which are found in nature, the material called cellulose is the most abundant. As the name implies, it is the chief constituent of the cells of plant tissues, and as a result it is widely distributed throughout the world Not all naturally occurring cellulosic materials, however, are of the same content of cellulose. Some fibrous plant tissues, notably ramie and cotton, contain a high percentage of the material, while substances such as wood may contain as little as 40% of cellulose. The non-cellulosic constituents consist principally of lignins, pectins, fats and waxes.

The principal sources of the natural cellulosic textile fibers are the s
hairs and the bast fibers. The most important seed hair is cotton
among the bast fibers are flax, jute, hemp, and ramie. Differences in
nature and content of both the cellulosic and non-cellulosic constitue
determine, to a large extent, the fiber chosen for a particular use. Tl
cotton, which is fairly high in cellulose content and which is easily purifi
finds use in fabrics for clothing, while ramie, although it contains a h
quality cellulose, is brittle, inelastic, and purified with great difficu
finds extremely limited use as a textile material. It is considered beyo
the scope of this writing to delve further into the various sources, pr
erties and uses of all the vegetable tissues which contain cellulose; a co
plete description of these aspects may be found elsewhere.[1]

Because of its abundance and high degree of purity and the ease
removal of non-cellulosic substances therefrom, the cotton fiber has be
the source of cellulose for most investigations dealing with the chemis
of this complex material. The experimental evidence at hand indica
that indeed there are no differences in chemical properties of purifi
cellulose from various sources, although there may be differences in *ra*
of reactivity of the groupings brought about by certain dissimilarities
physical structure.

The native or raw cotton fiber consists of a primary and a seconda
wall. The latter, which comprises the bulk of the fiber and the backbone
textiles made from cotton, consists practically entirely of cellulose. Tl
secondary wall is enclosed by the thin so-called primary wall made up
fine criss-crossing strands of cellulose embedded in a membrane form
principally of wax and pectic substance, the latter combined with catio
such as calcium, magnesium, sodium, potassium, iron, and aluminum. T
lumen, or central canal, which is prominent in many fibers, also contai
a small amount of these non-cellulosic constituents. The microscopic stru
ture is revealed in Figures 1 and 2, which show cotton fibers in longitudin
and cross-sectional view, respectively.[2]

During manufacturing, more or less of the non-cellulosic materials ma
be removed from the raw fiber depending upon the severity of the proce
employed. In the preparation of a fabric such as heavy duck for tarpauli
or awnings, the cotton itself is subjected to no chemical processing wha
soever and the resulting product contains, for all practical purposes, ra
cotton. On the other hand, fabrics for clothing, for reasons of ease

[1] "Cellulose and Cellulose Derivatives," edited by Emil Ott. Interscience Pu
lishers, Inc. (1943).

"Cellulose Chemistry," Emil Heuser. John Wiley & Sons, Inc. (1944).

"Introduction to the Chemistry of Cellulose," Marsh and Wood. Chapman
Hall, Ltd. (1942).

[2] Hock, C. W., Ramsay, R. C., and Harris, M., *J. Research Nat'l Bur. Standard*
26, 93 (1941).

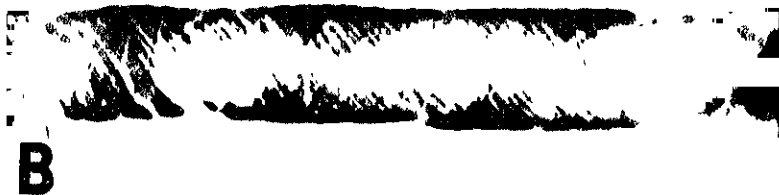
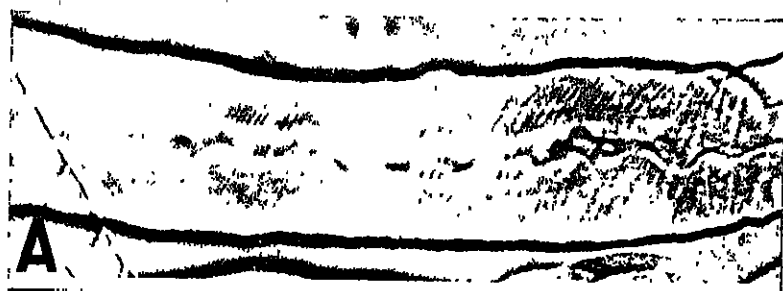



Figure 1 Mature fibers swollen to show the outer winding A, photographed in ordinary light; B and C, between crossed nicols C shows a reversal of the winding Magnification x420 (*Hock, Ramsey and Harris* [2])

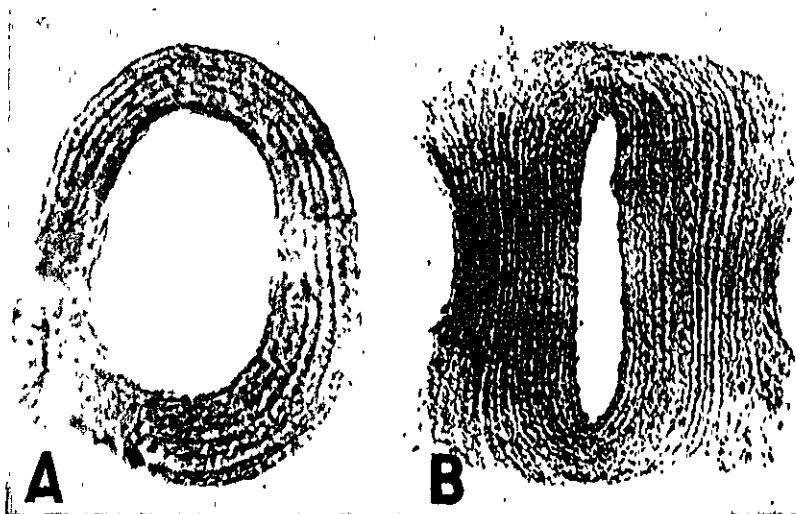
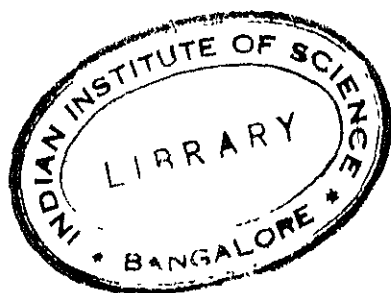
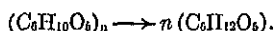
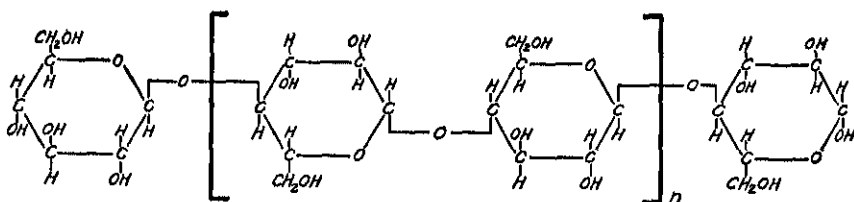



Figure 2. Cross section of cotton fibers swollen in dilute cuprammonium hydroxide solution to show "growth rings." A and B are 25-day and mature fibers, respectively. Magnification of A, x925; of B, x400. (*Hock, Ramsey and Harris*[2])

dyeing, fastness of color, etc., are thoroughly kier-boiled, bleached, soured and soaped, and the finished product is practically pure cellulose. The properties of either type of end product are, of course, intimately associated with the nature of the cellulose, and any changes in the latter brought about by one treatment or another are usually revealed in a change in properties of the fabric.

As early as 1842, it was recognized that cellulose was a constituent of wood, cotton lint, roots, and various other fibrous tissues, and that it was closely associated with the dextrorotatory sugar, glucose. Elementary analysis indicated the empirical formula $C_6H_{10}O_5$ and hydrolysis with mineral acid gave yields of glucose to the extent of at least 95% of the theoretical, assuming the conversion

$$(C_6H_{10}O_5)_n \longrightarrow n\,(C_6H_{12}O_6).$$

Without going into the details and experimental proof of the structure of cellulose,[3] it suffices to say that all evidence points to the formula

*Molecular formula for cellulose*

in which a large number of β-glucose units are joined together by means of oxygen bridges in the manner shown. These are referred to as 1, 4-glucosidic linkages, and arise by the elimination of the elements of water between the hemiacetal group on carbon atom 1 of one unit and the hydroxyl group on carbon 4 of the adjacent unit. The letter $n$ denotes the number of anhydro-glucose residues which occur between the two ends of the cellulose chains. This number is by no means a fixed one and in the various types of native cellulose it ranges from averages of about 1500 to 3000. The total number of units in a cellulose chain is referred to as its degree of polymerization (D.P.). This number may be calculated by dividing the molecular weight by 162, the weight of an anhydro-glucose residue. The cotton fiber, or any cellulosic fiber, however, does not contain a single chain, but is a composite of many chains which are most probably of different lengths. It is therefore heterogeneous with respect to molecular size, or polymolecular. Thus, when reference is made to the degree of polymerization of a cellulosic material, the value represents

[3] This may be found in review form in a paper by Freudenberg, K., and Blomquist, C., *Ber.*, 68B, 2070 (1935).

the average length of the many chain molecules of which it is comprised.

There are a number of methods available for the determination of the molecular weight of cellulosic materials. The classical ones used for low-molecular-weight organic compounds, however, cannot be applied and recourse is had principally to the viscosity, osmotic pressure, or end-group methods. The first of these, *i.e.*, the property of viscosity, is determined by the dissolution of the cellulose in a suitable solvent, usually cuprammonium hydroxide, followed by an ordinary viscometric measurement. The viscosity method is a relative rather than an absolute one and requires calibration. At the present time, the most reliable procedure for this purpose appears to be ultracentrifugal analysis. Thus, Kraemer [4] showed that the weight-average molecular weight as determined by the ultracentrifuge was proportional to the intrinsic viscosity for cellulose and some of its derivatives, and derived constants which could be used for the calculation of molecular weight from viscosity. (Recent work by Gralen indicates that for cellulosic materials of very high molecular weight, a strict proportionality between intrinsic viscosity and molecular weight does not apply.) The osmotic pressure method at present is practical for use on derivatives of cellulose only. The end-group procedure involves the determination of the quantity of either the aldehyde groups which occur at one end of the cellulose chains, or the tetrahydroxy glucose residues which occur at the other (see formula, page 15).

Since each of the above properties, *i.e.*, viscosity, osmotic pressure, or end-group content is a function of the average molecular weight, these quantities are useful in determining the extent of degradation of cellulose brought about by various treatments. Each method, however, has certain limitations. These will be discussed as the occasion arises. For the most part, the viscosity of cellulose in cuprammonium has been the most practical method for the evaluation of molecular weight.

It is not surprising that rather wide variations in molecular weights of native celluloses have been found. In general, the highest values are obtained by ultra-centrifugal methods, and the lowest by end-group methods. A critical comparison of all the different procedures is not possible, however, since the methods have been applied to different products.

The manner in which the cellulose chains are arranged in a fibrous material, *i.e.*, the nature of the molecular structure, has been a matter of controversy for some time. Notable contributions in this respect have been made by Sponsler and Dore,[5] Mark,[6] and Meyer and Misch.[7] The

[4] Kraemer, E. O., *Ind. Eng. Chem.*, 30, 1200 (1938).

[5] Sponsler, O. L., and Dore, W. H., Fourth Colloid Symposium Monograph, Chemical Catalog, New York (1926).

[6] Mark, H., *J Phys. Chem.*, 44, 779 (1940); Meyer, K. H., and Mark, H., *Ber.*, 61, 593 (1928); Kratky, O., and Mark, H., *Z. Phys. Chem.*, B36, 129 (1937).

[7] Meyer, K. H., and Misch, L., *Helv. Chim. Acta*, 20, 232 (1937).

generally accepted picture at the present time is represented in Figure 3. It is seen that the fibrous structure is made up of molecular chains of various lengths lying roughly parallel to the fiber axis, and that in some regions they lie more closely together and possess a higher degree of order than in others. Regions of close lateral packing where the chains are parallel are designated as "crystalline," and these are differentiated from amorphous areas which possess a lesser degree of order. The former produce the characteristic x-ray diffraction pattern of cellulose, while the latter introduces the general fogging which is almost always in evidence. Although it is not possible to draw a sharp line of demarcation between these two phases because of the merging of one into the other (brought about by the continuity of the cellulose chains), the bulk of most natural cellulosic fibers is thought to be "crystalline." Attempts have been made

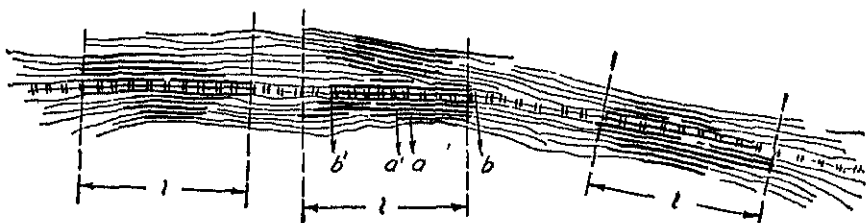



Figure 3. Schematic representation of cellulose crystallite structure showing how main valence chains pass through more than one micelle (fringe micellar theory). (*Mark* [6])

*a*, $a^1$, $b^1$, molecular ends inside the crystallized region of one micelle; *b*, molecule end outside the crystallized region; *l*, length of crystallized region.

to estimate the proportion of each by methods which involve the ease of reactivity of various chemical agents with the fibrous material [8] and, as might be expected, the values which have been obtained vary with the method employed.

Certain of the physical properties of fibers are believed to be related to the relative properties of crystalline and amorphous cellulose present. For example, the strength is contributed primarily by the more highly crystallized areas. The presence of a large proportion of the latter also leads to brittleness. On the other hand, there is ample evidence to indicate that the amorphous portions contribute principally to elasticity, and are involved in swelling, dyeing, and phenomena of a similar nature.[9] These less highly organized areas presumably react more readily with most chemical agents, a property which has been used to estimate the quantity of easily accessible regions in various types of cellulosic materials. The resistance of

[8] Nickerson, R. F., *Ind. Eng. Chem.*, 33, 1022 (1941); Goldfinger, G., Mark, H., and Siggia, S., *Ind. Eng. Chem.*, 35, 1083 (1943).

[9] Mark, H., *J. Phys. Chem.*, 44, 764 (1940).

highly ordered or crystalline spots to such a simple compound as hydrochloric acid has been demonstrated.[10]

It is rather obvious from Figure 3 that the length of the cellulose chains in a fiber will also have a profound effect on its strength, high strengths being associated with long chains. Thus, from a practical point of view, it is desirable during the processing of, for example, cotton materials to maintain as nearly as possible the original chain length of the cotton cellulose. In so doing, a fabric of high quality is attained.

## 2. Chemical Nature and Reactions of Cellulose

From a knowledge of the composition and structure of cellulose, it is readily seen that it is similar in nature to a polyhydric alcohol and to a polysaccharide. Its chemical reactions are therefore similar to that of simpler organic compounds of this type. It contains at one end of each cellulose chain a hemiacetal or potential aldehyde group, and at the other a hydroxyl group not present on the remaining anhydro-glucose residues. There is nothing unique about this hydroxyl group (which is in the 4 position), except that its presence makes possible the estimation of the average molecular weight through the determination of tetrahydroxy glucose. Two secondary hydroxyl groups are found in the 2 and 3 positions. The two may be considered as a single glycol group, and as will be seen later they sometimes react as one. Finally, each of the anhydro-glucose residues carries the primary alcoholic group characteristic of glucose.

The methods of analysis which are applicable to the simpler organic compounds are not always suitable for cellulose, primarily because of the lack of sufficient sensitivity. For example, the hemiacetal or potential aldehydic reducing group at one end of the cellulose chain might be expected to undergo reactions characteristic of this group. Indeed it does, but the number of these groups in, for example, several grams of cellulose is so small that their detection by ordinary methods is extremely difficult. Another difficulty arises from the fact that cellulose is insoluble, and the reactions must take place in a heterogeneous system.

With respect to the alcoholic nature of cellulose, most of the reactions involve the formation of derivatives, *i.e.*, the adding-on to the chain molecule a group or groups to create certain characteristics not present in cellulose itself. Such processes are involved in the formation of alcoholate-like compounds, ethers (ethyl cellulose) and esters (cellulose acetate), all of which have wide commercial application.

Inorganic esters of cellulose such as cellulose nitrate, sulphate, and phosphate are well known and are not difficult to prepare. The first of these, however, is the only derivative of this type which at present has

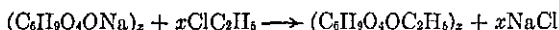
[10] Davidson, G. F., *J. Textile Inst.*, 34, T87 (1943).

any commercial significance. The phosphate promises to assume some importance, particularly in the formation of flame-resistant cellulose. The preparation of any of these derivatives involves straightforward organic chemistry, except that conditions must be well controlled in order to minimize effects which tend to reduce the length of the chain molecules.

One of the oldest and most important commercial reactions of cellulose involves the formation of a complex with alkalis. In 1844, Mercer noted that the properties of cellulose became radically changed when it was treated with 12 to 18 per cent sodium hydroxide, and since then many researches have been conducted to elucidate the nature of the chemical reaction. In spite of this, controversy still exists as to whether a true alcoholate, cellulose-O-Na, is produced or whether the sodium hydroxide forms an addition complex of the type $(\text{cellulose-OH})_x \cdot (\text{NaOH})_y$. In any event, the formation of the so-called soda cellulose finds extensive commercial application since the compound serves as an intermediate in the preparation of many derivatives. An example may be cited in the preparation of ethyl cellulose: the raw material is first treated with aqueous alkali to form soda cellulose

$$(C_6H_{10}O_5)_x + x\text{NaOH} \longrightarrow (C_6H_9O_4ONa)_x$$

and this is then reacted with, for example, ethyl chloride

$$(C_6H_9O_4ONa)_x + x\text{ClC}_2H_5 \longrightarrow (C_6H_9O_4OC_2H_5)_x + x\text{NaCl}$$

to form ethyl cellulose. The reaction is not unlike the preparation of ethers from aliphatic alcohols. The production of viscose rayon also utilizes as the first step the formation of soda cellulose which is subsequently xanthated with carbon bisulphide and then regenerated. Although commercially the formation of ethers of cellulose utilize soda cellulose as an intermediate, the alcoholic hydroxyls will react directly with ethylene oxide, diazomethane, and with sodium metal in liquid ammonia.

With respect to the process of mercerization, which involves treatment for a very short period of time with about 18% sodium hydroxide, the principal effects on cotton are to swell the fibers longitudinally, shrink them laterally, and give them a greater absorption of water, dyes, etc., as well as in increased chemical reactivity. When the treatment is carried out under tension, the fibers also acquire a smooth lustrous surface and exhibit an increase in strength. The increase in absorptive power and reactivity is ascribed to the formation of amorphous areas in the cellulosic structure at the expense of the crystalline portions.

Unlike the reactions of cellulose with sodium hydroxide, the formation of other metal alcoholates have no commercial value. From an academic point of view, however, studies of the reactions of such compounds as thallous ethylate to form the thallium alcoholate of cellulose has been of use in elucidating the structural characteristics of cellulosic materials. By

a clever method of analysis, the area of the internal surface or the num of available surface hydroxyl groups may be determined.[11]

Finally, the formation of cellulose complexes, which is in all probabi associated with the alcoholic nature of cellulose, cannot be overlook Cuprammonium hydroxide solutions are the best known solvents for lulose, and the complex which is formed not only finds an academic us evaluating molecular size, but serves as an intermediate in the prepa tion of cuprammonium or Bemberg rayon. Certain other organic ba such as dibenzyl-dimethylammonium hydroxide are excellent swell agents and fair solvents for cellulose. Compounds of the tetraalkyla monium type have a potential value in that they dissolve cellulose permit the preparation of derivatives in a homogeneous medium inst of a heterogeneous one, as in the case of the inorganic bases.

The alcoholic groups also enter into reactions which are sometin detrimental to cellulosic materials. These involve oxidation of either both the secondary and primary alcohol groups to aldehyde or carbo groups. A detailed discussion of degradation by oxidation follows Section B.

The reactions characteristic of polysaccharides invariably involve shortening of the cellulose chains, *i.e.*, hydrolysis of glucosidic linkag by the addition of water. This effect may be brought about directly the use of acids, or it may result as a secondary process from activati of the glucosidic bond through oxidation of one or more of the hydrox groups. The intermediates between high molecular weight cellulose a glucose which are formed by this process also possess the properties polysaccharides. That is to say, cleavage of the oxygen bridges betwe glucose residues lowers the chain length, but does not essentially alter t chemical properties.

## B. NORMAL DEGRADATION REACTIONS[12]

*Henry A. Rutherford*

Cellulosic substances are readily degraded by acids, oxidizing agent enzymes, heat, and light. With rare exceptions, the processes of breal down are complicated and the chemical mechanisms of the reactions a not completely understood. This is particularly true of attack by en zymes, heat, and light, and it is not surprising when the chemical natu and structure of cellulose are considered. Not only are there a number vulnerable points in the molecule, but the accessibility of these points

[11] Harris, C. A., and Purves, C. B., *Paper Trade J.*, 110, 29 (1940).

[12] For a more comprehensive treatment of the degradation reactions of cellulos see the author's sections in "Cellulose and Cellulose Derivatives," edited by Em Ott, Interscience Publishers, Inc., New York (1943).

limited by the physical arrangement of the groupings and by the insolubility of the cellulosic material. Thus, it is expected that most chemical reactions would follow a heterogeneous course. Because of this, it has not been possible to develop with any degree of certainty the theoretical aspects of cellulose degradation. Theoretical considerations have been presented in recent literature principally by Mark, Meyer, Freudenberg, Kuhn, and Simha,[13] but no conclusive experimental evidence is yet available to support the relations in a quantitative way. It is the purpose of this section to describe only those chemical degradation reactions of cellulose which are understood best, and to review briefly the properties of celluloses modified by various chemical means.

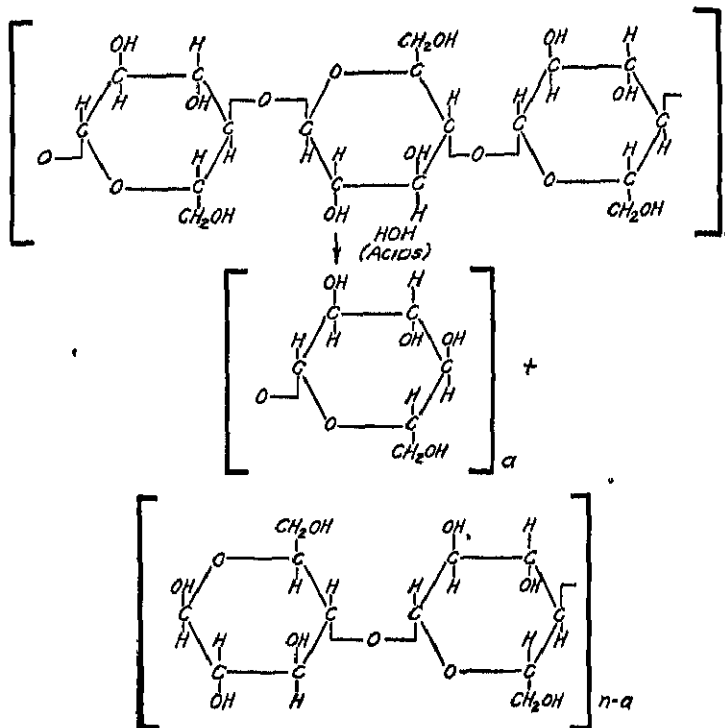
### 1. Hydrolysis of Cellulose

When a cellulosic material is subjected to the action of an acid, particularly one of the mineral acid series, a hydrolytic type of breakdown which involves a simple cleavage of 1, 4-glucosidic linkages occurs The result of such an action is a shortening of the cellulose chain to produce fragments having lower average molecular weights than that of the untreated cellulose. The reaction is essentially a reversal of the procedure by which the chains are built up, and may be represented by the scheme given on page 22.

If the reaction is allowed to proceed far enough, glucose and a small amount of its acid decomposition products are the final substances obtained. For the reasons mentioned above, the degradation does not take place in a uniform manner and if the reaction is stopped prior to completion, the partially hydrolyzed cellulose may be divided into a number of fractions, the molecular weights of which may vary between that of glucose and the original material itself. Thus, the degradation product consists of a homologous series of celluloses in which the macromolecules may have arrangements similar to those in the original material, but are nonhomogeneous in character and exhibit lower average molecular chain lengths than the original cellulose. This mixture of cellulosic substances obtained by the action of acids is referred to by the generic term "hydrocellulose." Hydrocellulose is thus not a homogeneous chemical entity, as earlier investigators believed.

Girard[14] was one of the earliest investigators to find that hydrocellulose could be prepared by a number of methods. He was able to produce a series of white, friable powders by immersion of cellulose in mineral acids,

[13] Meyer, K. H, Hopff, H, and Mark, H, *Ber*, 62B, 1103 (1929); Montroll, E. W., and Simha, R., *J. Chem. Phys.*, 8, 721 (1940); Simha, R., *J. Applied Phys.*, 12, 569 (1941).

[14] Girard, A., *Compt. rend.*, 81, 1105 (1875); 88, 1322 (1879); *Ann. Chim. Phys.*, 24, 337 (1881).

*Molecular reaction showing the hydrolytic breakdown of cellulose in the presence of an acid.*

by the action of moist gaseous halogen acids, or by impregnating the fil with solutions of certain organic acids and then heating the materials 100° C. The organic acids are found to produce tendering at a slower r than the mineral acids. This appears to be related to the fact that former are weaker acids.

Birtwell, Clibbens and Geake [15] were the first to make a thorough stu of the factors which influence the rate of hydrolysis of cellulose by aci Primarily, the rate is a function of the kind of acid, its concentration, a the temperature. By the proper control of each condition, it is possible duplicate with a fair degree of precision the preparation of a hydrocel lose of given physical and chemical properties.

Two of the most characteristic changes which accompany the degrac tion by acids are a decrease in viscosity and in strength of the cellulo As stated in Section A above, both of these properties are dependent to considerable extent upon the average length of the cellulose chain mo cules, and it is not surprising that a definite and practically constant re tion between loss in strength and decrease in viscosity is found. This rel

[15] Birtwell, C., Clibbens, D. A., and Geake, A., *J. Textile Inst.*, 17, T145 (1926)

tionship, expressed in terms of the reciprocal of viscosity, namely, the fluidity,[16] is emphasized in Figure 4. The unique feature of this relationship is that it is independent of the nature and conditions of the acid treatment, and it obtains for a pure cellulosic fiber, yarn, or fabric. Results of this kind lead to the conclusion that the degradation of cellulose by acids during the early stages of attack is fairly uniform over the chain molecules, and that the glucosidic linkages are broken more or less at random. Highly localized attack on cellulosic fibers could result in a large

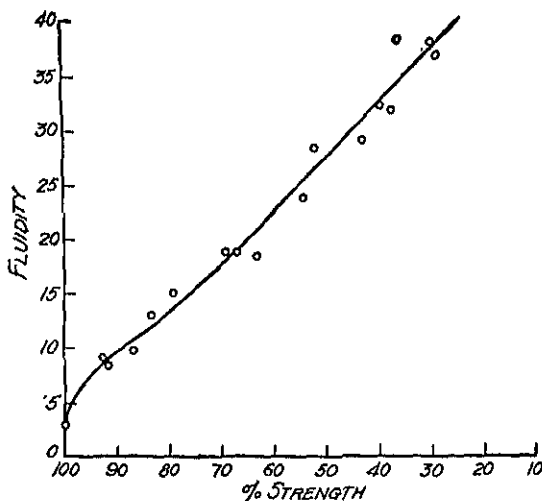



Figure 4. The relation between breaking strength and fluidity of hydrocelluloses. (*Clibbens and Ridge* [17])

loss of strength without an accompanying appreciable increase in fluidity.

Although from a practical point of view, the most important aspects of cellulose degradation are in the early stages of attack, a number of investigations have been directed toward an examination of the properties of cellulose after prolonged treatment with acidic substances. In a heterogeneous system, it is invariably found that the rate of reaction as shown by the properties of, *e.g.*, strength and fluidity, takes place rapidly at first (*i.e.*, during the early stages) and slows down considerably as the duration of treatment is prolonged. It is of interest that, judged by some properties of the residual cellulose, the hydrolysis appears to stop short of completion. Thus, for example, the fluidity of cotton cellulose in cuprammonium reaches a maximum of about 50 upon treatment with hydrochloric or sulphuric acid instead of the maximum value possible, about 63. This

[16] As a matter of convenience in referring to viscosity characteristics, the term "fluidity," which is the reciprocal of viscosity, was introduced. The use of this term is commonly employed in the description of textile materials.

[17] Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, 19, T389 (1928).

is shown by the results obtained by Davidson [10] (Figure 5). When 1
cerized cotton was treated in a similar manner, a maximum fluidit
about 60 was attained. The degrees of polymerization calculated 1
Kraemer's constants, which correspond to fluidities of 50 and 60,
spectively, are 190 and 95. Thus, the degradation is far short of b
complete, particularly in the unmercerized cotton. These results, in a
tion to the observation that the x-ray diagram of the powdery res
was identical with the original cellulose, indicate that the acid does
penetrate the crystalline portions of the fibers and that the actio
confined to hydrolysis of glucosidic linkages situated in the amorpl

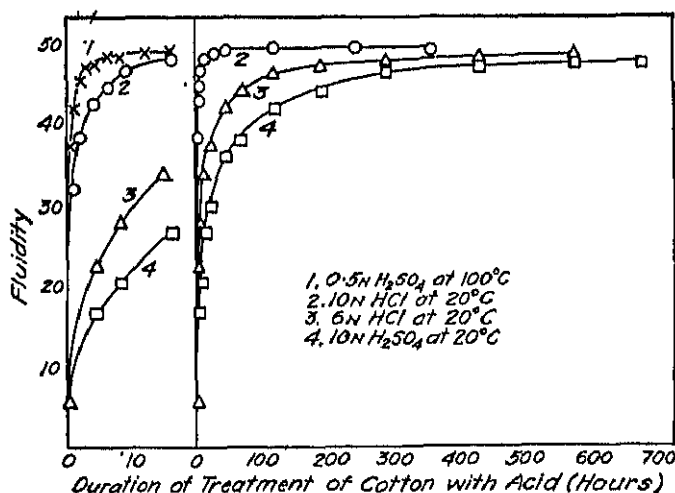



Figure 5. The effect of inorganic acids upon fluidity, showing both the extent and relative rates of attack. (*Davidson* [10])

regions. It is generally assumed that mercerization increases the cont
of amorphous areas in cotton, and the higher rate of hydrolysis found w
the mercerized as compared with the unmercerized supports this view

Although other properties such as solubility in alkali and moisture a
sorption also reach an approximately constant value after prolong
hydrolysis, it should be emphasized that the action does not entirely cea
but continues extremely slowly. Ultimately, even in a heterogeneous sy
tem, the cellulose is completely destroyed.

A more complete study of the relation between strength and degree
polymerization of cellulose degraded by acids was made by Stauding
and Sorkin.[18] It was found that materials having D.P.'s of 200 to 250 d
integrated on handling, while in the range of 250 to 700 both the breaki
strength and the elongation at the break increased with increase in D.

[18] Staudinger, H., and Sorkin, M., *Ber.*, 70B, 1565 (1937).

Further increases beyond 700 resulted in only slight further improvement in these properties.

An obvious result of the shortening of the cellulose chains in the manner indicated above is a production of new aldehydic end groups. Accordingly, another characteristic change which accompanies the formation of hydrocellulose is an increase in reducing properties. The presence of these groups is shown by the reducing action of hydrocellulose on copper (*e.g.*, Fehling's solution), ammoniacal silver nitrate, and by reaction with phenylhydrazine, hydroxylamine, Schiff's reagent and ethyl mercaptan. The most commonly used method for determining this type of end group has been the well-known "copper number" method developed originally by Schwalbe.[10] The method depends on the reduction of copper from the cupric to the cuprous state by the cellulosic material. The original procedure has been frequently modified, but, despite numerous improvements, it still leaves much to be desired. Thus, the copper number obtained for a particular sample has been shown to depend on such factors as temperature of heating, time of heating, ratio of weight of sample to weight of solution, physical state of the sample (fineness of cutting or grinding), composition of the solution containing the cupric ion, solubility of the $Cu_2O$ formed in the mother liquor, and the progressive degradation of the cellulose by the alkaline solutions employed For these reasons, the copper number at best can be considered to be only a rough measure of the content of reducing groups of a cellulosic material. The results obtained by this method, however, have more significance when it is applied to a homologous series of samples prepared by similar treatments. Thus, some interesting relationships are obtained between copper number and *e g*, viscosity of hydrocelluloses. It has been shown that when the copper number lies within the limits of 0.3 and 4.0, its relationship to viscosity can be expressed by the equation $N_{Cu}V^2 = 2.6$ where $N_{Cu}$ is the copper number and $V$ is the log of the relative viscosity.

The validity of the chemical mechanism of hydrocellulose formation is further demonstrated by the direct relation between aldehydic reducing groups, determined by a method specific for these groups, and fluidity The relationship for a series of hydrocelluloses down to molecular chain lengths which correspond to almost total loss in strength of cotton fibers is shown in Figure 6.

The decrease in molecular size of cellulose during degradation with acids is also accompanied by an increase in solubility, especially in alkaline solutions. However, even boiling water dissolves a fraction of hydrocellulose which is higher in reducing power than the original hydrocellulose. When hot dilute solutions of alkalies are used, additional soluble decomposition products are obtained. The loss in weight, the effect on

[10] Schwalbe, C. G., *Ber.*, 40, 1347 (1907).

fluidity and breaking strength, and the change in copper number of hydrocelluloses on boiling in alkaline solutions has been rather extensively investigated. In general, it has been found that the reducing power of the hydrocellulose on treatment with hot alkali is decreased and may even fall to nearly zero without necessarily being accompanied by extensive weight losses. The solubilities in alkali of hydrocelluloses appear to be related to the reducing power of the material; that is, hydrocelluloses of the same copper number have been shown to have the same solubility. On boiling in alkaline solutions, they sometimes exhibit a considerable loss in weight without undergoing a large change in fluidity, and in this respect they differ from most other types of modified celluloses.

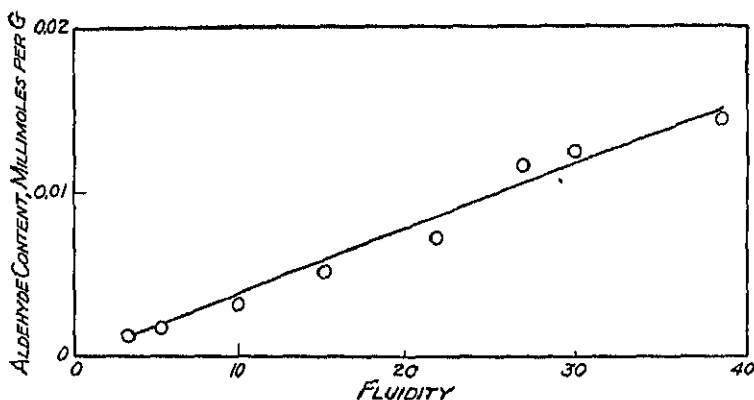



Figure 6. Relation of aldehydic content of hydrocelluloses to fluidity. (*Martin, Smith, Whistler, Harris*[20])

The practical aspects of degradation of cellulose by hydrolysis were brought out a number of times during World War II. It was perhaps emphasized more during this period because of the many treatments which were developed to give cotton fabrics certain desirable characteristics or to prolong their useful service life. One such treatment was employed in the production of the so-called Duck, Cotton; Fire, Water, Weather, and Mildew Resistant. Studies of the mechanism of deterioration of this type of fabric revealed that in many instances the chlorinated paraffin present in the finish was unstable to heat and/or light, and liberated hydrogen chloride. In the presence of moisture, this compound had an adverse effect on the cotton, the severity of attack depending upon the conditions which prevailed at the point of usage. An examination of the strength-fluidity

[20] Martin, A. R., Smith, L., Whistler, R. L., and Harris, M., *J. Research Nat'l. Bur. Standards*, 27, 449 (1941); *Am. Dyestuff Reptr.*, 30, 628 (1941).

relationships of damaged tentage sometimes gave results which were similar to the relation shown in Figure 4 for hydrocelluloses. This was regarded as strong evidence that the breakdown was caused by hydrolysis of the cellulose and not by some other means. (See Chapter VII, Section A, 2-b.) This knowledge lent a scientific background for the incorporation of basic substances in the finish for the purpose of absorbing HCl, thus preventing the attack on the cotton. Experience with this fabric has shown that the durability was greatly improved after the use of basic substances by the finishers became widespread.

In view of the well-known sensitivity of cellulose to acids, it is safe to say that any flameproofing treatment for cotton textiles should not leave an excessive acidic residue on the fabric. Some rather extensive studies have been carried out to reveal the level of acidity at which cotton begins to deteriorate rapidly. Obviously, there is no definite answer to this question because of the dependence of rate of breakdown on the severity of other conditions (*e.g.*, temperature). However, it appears that fabrics which are to be subjected to outdoor weathering or to elevated temperatures indoors should not give water extracts which are below pH 6.0.

### 2. Oxidation of Cellulose

In contrast to hydrolysis, the oxidation of cellulose is an extremely complicated process, and results in the formation of a wide variety of modified celluloses, the structures of which are not known in the majority of cases. The reaction products are, in general, heterogeneous with respect to both structure and molecular size and do not constitute chemical entities For this reason the term "oxycellulose" has no meaning other than to identify a cellulosic material which has been attacked by an oxidizing agent. The need for more specific terms to identify the products has been recognized, and there are indications that a system of nomenclature is forthcoming To avoid confusion, however, the present discussion will follow the conventional methods of designating the products of oxidation.

From a technical point of view, the oxidation of cellulose is a subject of great importance. In the commercial processing of cellulose, for example, bleaching treatments are frequently required to remove the colored substances which impart a yellowish tint to the material; in such treatments, oxidizing agents such as hypochlorite or hydrogen peroxide may be employed, and unless care and control are exercised, severe tendering of the cotton cellulose, due to oxidative degradation, may occur. Cellulose is also readily degraded by oxygen in strongly alkaline solutions, a reaction which is utilized in the preparation of viscose rayon.

The properties of any oxycellulose depend upon the method by which it is prepared, but in general it may be said that in neutral or acidic solu-

tions, oxycelluloses of the *reducing* type are formed (*i.e.*, they
high content of reducing groups as measured by the copper
method), whereas in alkaline solutions, the *acidic* type of oxycel
formed. The latter has sometimes been referred to as the "methyle
type since it exhibits rather high affinity for methylene blue. Aci
celluloses tend to show high retention of alkali presumably du
presence of carboxylic acid groups.

The manner in which hydrogen-ion concentration may influe
rate or type of oxidation has been extensively studied by m
vestigators. Oxidation generally proceeds most rapidly near pH
for this reason neutrality is always avoided in the commercial bl
of cotton. This is shown for oxidation by chlorine solutions in Fi
and 8. The data also emphasize the fact that the rate or extent o
tion is not necessarily ascertained by the measurement of the ch
any one given property such as copper number or methylene blue
tion; thus, as indicated by the copper number method, the rate is
at pH 4.6 than at pH 11.2, whereas, as indicated by methyle
absorption, the effects of pH appear to be reversed.

The rate of oxycellulose formation is also influenced by temp
concentration of oxidant, and the nature of the oxidizing reagen
As an example of the last, hypobromite is much more effective for
set of conditions than hypochlorite. Finally, the rate of oxidation
cellulose may be greatly accelerated by the presence of another oxi
substance in the system. Thus, oxidation with dichromate in the p
of oxalic acid is far more rapid than in the presence of sulfuric a
another example, it has been shown that when cotton, on which a r
vat dye has been absorbed, is treated with hypochlorite, the oxida
the cellulose is greatly accelerated.

The extensive literature on oxycellulose is indicative of the en
amount of work which has been done in this field and yet, at the p
time, it must be concluded that the chemical mechanism of oxidat
tack by most reagents is not clearly understood. It would appear th
attack on cellulose would be confined to three points in the anhydrog
residue of the cellulose chain: (1) The aldehydic end groups, of
there are few if any in native cellulose, could be oxidized to ca
groups. Such a process would not be expected to result in sign
changes in the properties of celluloses of high average chain length
might alter considerably the properties of an appreciably degraded l
cellulose. (2) The primary alcohol groups could be oxidized to the
hyde or carboxylic acid depending upon the oxidizing conditions.
oxidations would lead to a reducing type or an acidic type of oxycell
depending upon whether the reaction proceeded to the aldehyde or
acid. (3) The glycol group (the 2,3-dihydroxy group) of the glucose
due could be oxidized with the formation of ketonic, aldehydic, or

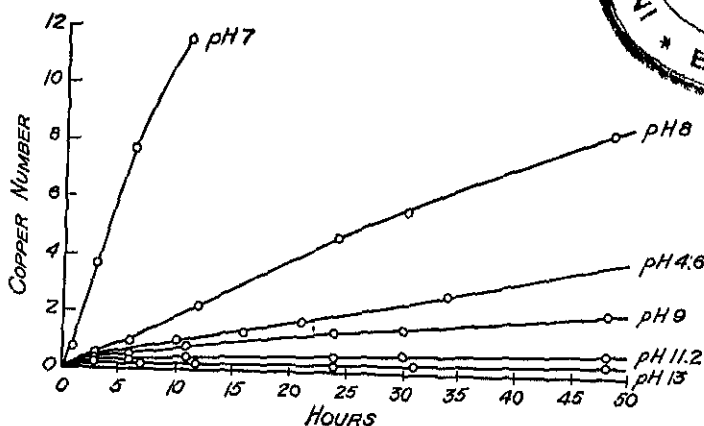
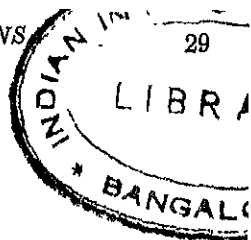



Figure 7. The effect of pH on the rate of increase of copper number. (*Clibbens and Ridge*[21])

0.04 $N$ sodium hypochlorite at 25° C.; ratio of cotton to solution 1:100.

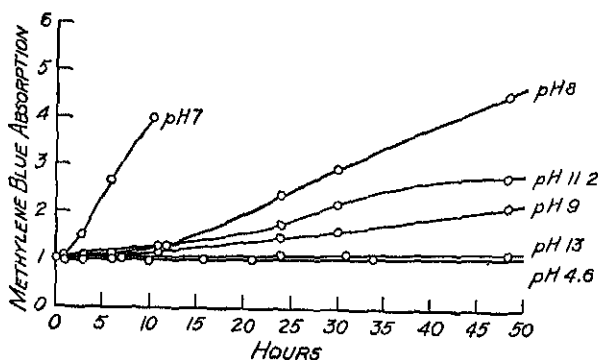
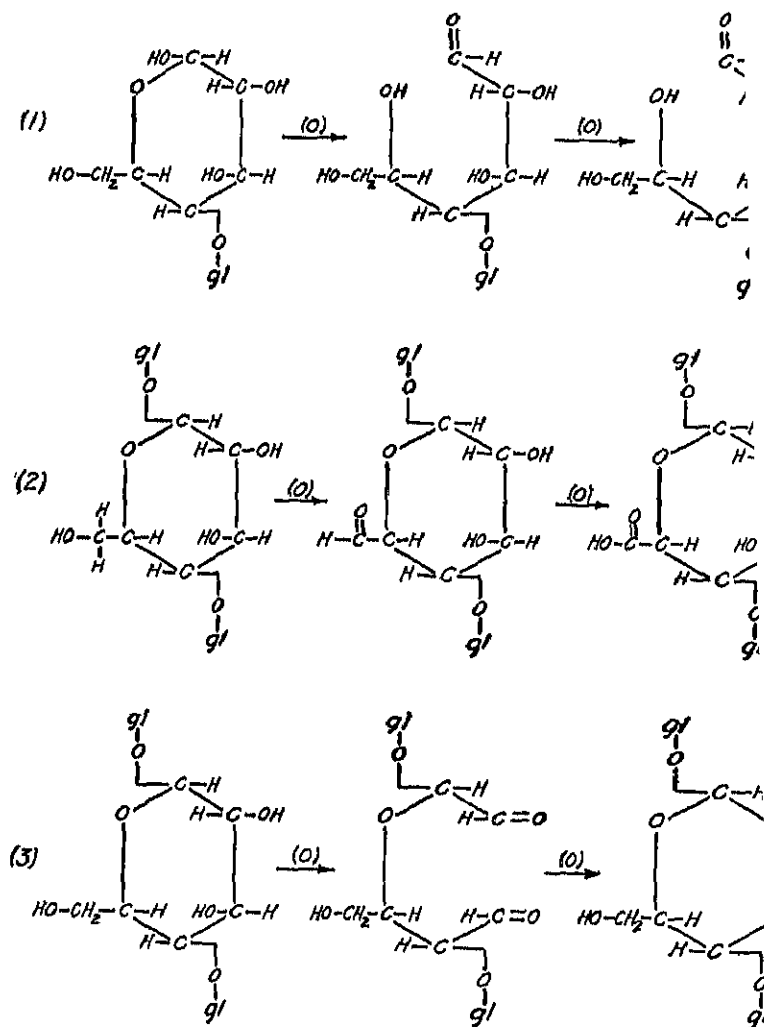



Figure 8. The effect of pH on the rate of increase of methylene blue absorption (*Clibbens and Ridge*[21])

0.4 $N$ sodium hypochlorite at 25° C; ratio of cotton to solution 1:100.

[21] Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, 18, T135 (1927).

boxylic groups, depending upon the course of the reaction. The
tions may be represented by the following formulae:

*Molecular reactions showing the oxidation of cellulose at*

*(1) the aldehydic end group;*
*(2) the primary alcohol group;*
*(3) the glycol group.*

A major difficulty in most attempts to ascertain the course of the
tion of cellulose has been the lack of analytical methods of su
specificity and sensitivity to determine accurately the number of
the above-mentioned groups which might be formed, or to allocat
to their positions in the glucose residues. The limitations of such m
as those involving the measurement of copper number as an estim

reducing groups or methylene blue absorption as an estimate of acidic groups are well recognized, and quantitative conclusions based on their use may be open to criticism. Nevertheless, considerable use has been made of them and they have been helpful in obtaining a rough qualitative picture of the course of some of the reactions. More recently, a number of new methods for the estimation of aldehydic and carboxylic groups in cellulose have been developed and are at present being applied to quantitative studies of the functional groups in various types of oxycelluloses.

Until recently, it was widely assumed that the oxidative attack occurred at the primary alcohol groups in the cellulose chain molecules causing either weakening or actual scission of the glucosidic linkages. In favor of this assumption was the fact that many of the oxycelluloses yielded carbon dioxide during boiling with hydrochloric acid, a reaction which is characteristic of uronic acids. Oxidation of the primary alcohol group to the carboxyl group stage would result in the formation of a glucuronic acid anhydride residue. Unfortunately, the hypothesis of simple oxidation of the primary alcohol group to one of a carboxylic acid type does not adequately explain the behaviors of all of the various types of oxycelluloses. Thus, Clibbens and Ridge [22] have shown that, whereas there is a proportional increase in cuprammonium fluidity and in copper number with decrease in tensile strength for hydrocelluloses, regardless of the type of acid used in their preparation, this proportionality does not exist for all types of oxycellulose. The data in Table 1 illustrate this point. Similarly,

Table 1. Relation Between Cuprammonium Fluidity and Strength of Hydrocellulose and Different Types of Oxycelluloses (Clibbens and Ridge) [22]

| | Percentage loss of strength (single-thread breaking load) | | | |
|---|---|---|---|---|
| Cuprammonium Fluidity | Caused by Acid Attack | Caused by Attack with Hypochlorite or Hypobromite | Caused by Attack with Dichromate plus $H_2SO_4$ | Caused by Attack with Dichromate plus Oxalic Acid |
| 10 | 10 | 7 | 2 | 1 |
| 20 | 34 | 25 | 11 | 6 |
| 30 | 58 | 47 | 26 | 16 |

no relationship exists between copper number and tensile strengths for all types of oxycellulose For example, a rise of one unit in copper number may correspond to complete loss in strength as in the case of alkaline hypochlorite modification, to 50% loss as in tendering by acids, or to practically no loss in strength as in the oxidation with dichromate. Since, on the basis of the molecular chain theory, both the fluidity and the tensile strength of cellulose are regarded as functions of chain length, this apparent anomaly was at first disturbing.

As a solution of this difficulty, Davidson [23] suggested that some types of oxidation do not result in direct scission of the chain molecules but reduce the chemical stability of some of the linkages in the cellulose chain

[22] Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.*, 19, T389 (1928).
[23] Davidson, G. F., *J. Textile Inst.*, 29, T195 (1938).

toward alkalies. This suggestion was based on the discovery of
and Ridge that the changes in fluidity and strength after boiling
loses in alkaline solutions were such that the fluidity-strength rel
the same for all types of oxycellulose. Types of oxidation whic
rupture the chain would not have an appreciable effect on str
the same time, these types of modification result in a material
labile toward alkali and accordingly the fluidity in cuprammoni
tion will be high. This, then, would explain the apparent lack of
tion between strength and fluidity for all types of oxycelluloses.

On the basis of this reasoning, Davidson further postulated th
fluidity of this type of oxycellulose could be determined without
of alkaline solutions, then it would be possible to obtain a true

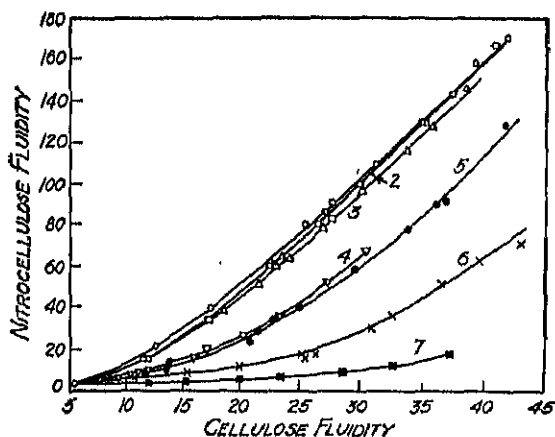



Figure 9. Relation between nitrocellulose fluidity and cuprammonium fluidity of modified cottons. (*Davidson*[28])

1 Hydrochloric acid.
2. Alkaline hypobromite.
3. Alkaline hypochlorite.
4. Acid hypochlorite.
5. Neutral hypochlorite.
6. Dichromate + sulfuric acid.
7. Dichromate + oxalic acid

of the average length of the molecular chains as they exist in th
Fortunately, it was found possible to do this by first nitrating t
luloses and then determining the fluidity of the derived nitrocellul
acetone or butyl acetate solution. By this procedure, it was fou
discrepancies between strength and fluidity (*i.e.*, oxycelluloses wh
hibit high strength and high cuprammonium fluidity) disappeared
oxycelluloses of the type characterized by high strengths also show
nitrocellulose fluidities.

From the foregoing, it is readily seen why the relationship of cu
monium to nitrocellulose fluidity as found for all types of hydrocel
does not exist for all types of oxycelluloses (Figure 9). If, howev

oxycelluloses are first boiled in alkaline solution, in order to complete the scission of the cellulose chains at or near the alkali-labile linkages, the nitrocellulose and cuprammonium fluidities change to a greater or less extent depending on the type of oxidative modification, and the relation

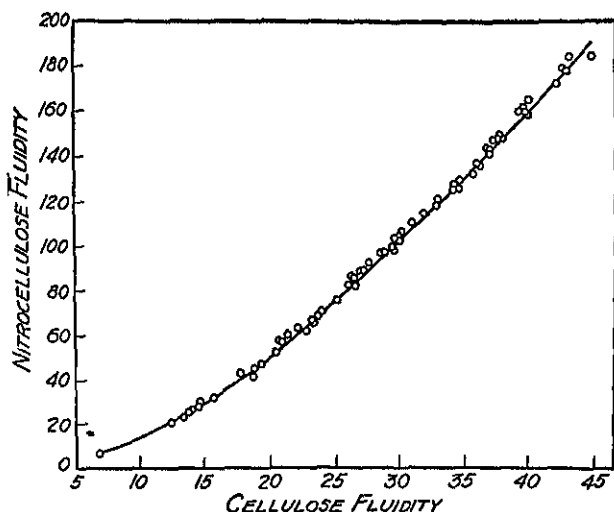
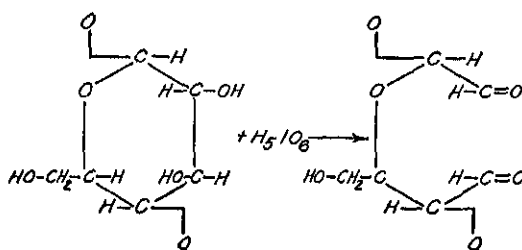



Figure 10 Relation between nitrocellulose fluidity and cuprammonium fluidity of modified cottons after boiling with sodium hydroxide solution. (*Davidson*[28])

between the two fluidities can then be expressed by a single curve as shown in Figure 10. These experiments left little doubt that the reducing types of oxycellulose do contain alkali-sensitive linkages.

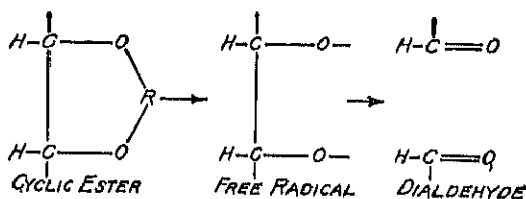
Davidson's hypothesis received considerable support from the investiga-

$$+ H_5IO_6 \longrightarrow$$

*Molecular reaction showing the oxidation of cellulose by periodic acid.*

tions of Jackson and Hudson who showed that in the oxidation of cellulose by periodic acid, cleavage of the glucose ring of the cellulose chain between carbon atoms 2 and 3 occurred with the conversion of the secondary alcoholic groups to aldehydes, according to the scheme above.

Subsequent to the work of Jackson and Hudson, the oxidation of cellulose by periodic acid has been studied extensively by Davidson,[24] and more recently by Rutherford, Minor, Martin and Harris,[25] and by Purves and coworkers.[26,27] By carefully controlling the conditions, it is possible to confine the reaction to the oxidation of the secondary hydroxyl groups to aldehyde groups in accordance with the above equation. Thus, it can be shown quantitatively that two moles of aldehyde groups are produced for each mole of oxidant consumed. Further, the reducing groups of the periodic acid oxycelluloses can be converted to carboxyl groups, the direct titration of which provides an independent check on the content of the former.[25]

The theoretical consideration of this type of oxidation reaction has led to some interesting results, and has enabled a prediction of the types of oxidizing agents which would effect a similar dialdehyde cleavage of cellulose.[27] Briefly, the requirements of the oxidant are as follows: (1) The central atom of the oxidant must have a diameter of about 2.5 to 3.0 Å, which is large enough to bridge the space between the hydroxyl groups in a 1,2 glycol (in the case of cellulose, the hydroxyl groups in the 2 and 3 positions). It must also be able to coordinate at least two hydroxyl groups in addition to the groups already attached to it. This enables the formation of an intermediate cyclic ester, as shown below, where *R* contains the central atom:

CYCLIC ESTER → FREE RADICAL → DIALDEHYDE

*Molecular reaction showing oxidation of cellulose glycol group through the stages of cyclic ester, free radical, dialdehyde.*

(2) The valence of the central atom must exceed by two units the valence of the next lowest stable state, and the oxidant should have a standard $E_0$ oxidation potential of about − 1.7 volts with respect to the next lowest stable state. With these provisions, the valance of the central atom is reduced to form a free radical which rearranges to produce the dialdehyde as shown above.

[24] Davidson, G. F., *J. Textile Institute*, 31, T81 (1940); 32, T109 (1941).

[25] Rutherford, H. A., Minor, F. W., Martin, A. R., and Harris, M., *J. Research Natl. Bur. Standards*, 29, 131 (1942).

[26] Heidt, L. J., Gladding, E. K., and Purves, C. B., *Paper Trade J.*, 121, 81 (1945).

[27] Grangaard, D. H., Gladding, E. K., and Purves, C. B., *Paper Trade J.*, 115, 41 (1942).

It is of interest that common oxidants such as nitric acid, hypochlorite, dichromate, and permanganate do not have all the properties regarded as necessary for the dialdehyde type of oxidation and these are not known to oxidize cellulose in this manner. In fact, certain properties of celluloses modified by these agents make it clear that the mechanism does not follow that of periodic acid. In addition, oxycelluloses, which on the basis of certain criteria are of the same type, have been found to yield products which vary considerably in other properties. Thus, Davidson [28] has recently compared the properties of oxycellulose prepared with chromic acid and periodic acid and has observed rather profound differences in their behavior, although both reagents give reducing oxycelluloses as determined by the copper number method. He suggests that the cellulose is more uniformly attacked by the latter reagent, whereas the action of chromic acid is limited primarily to the noncrystalline regions. Supporting this suggestion is the fact that the x-ray patterns are not destroyed by a high degree of oxidation with chromic acid, whereas periodate gradually destroys the characteristic x-ray diagram of cellulose.

A different explanation for the behavior of chromic acid toward cellulose has been put forth by Staudinger and Sohn, who suggest that glucosidic linkages are converted to carbonic ester linkages, such linkages accounting for the alkali-lability of oxycellulose. However, as already pointed out by Davidson, a similar reason could be given to explain the mechanism of oxidation by periodic acid, which produces oxycelluloses that are even more alkali-labile than chromic acid oxycelluloses.

Another mechanism of oxycellulose formation which has been advanced involves as a primary reaction the splitting of 1,4-glucosidic linkages This cannot be considered to be a general reaction since oxidations can occur under conditions which do not produce significant changes in chain length

A very different type of oxidation has recently been described by Kenyon and his coworkers [29] who used nitrogen dioxide as the oxidizing agent. In contrast with most types of oxidations, which when carried to excess result in complete disintegration of cellulose fibers, it was found that at any stage of oxidation with nitrogen dioxide, the cellulose still retains its fibrous structure. Of especial interest, however, is the fact that the oxidation appears to be confined entirely to the primary alcoholic groups and results in the conversion of these groups to carboxylic acid groups. Oxycelluloses having carboxyl contents which approached theoretical values calculated on the assumption that all primary alcoholic groups have been oxidized were prepared by these investigators.

The effects of another gaseous oxidizing agent, ozone, have been in-

[28] Davidson, G. F., *J. Textile Inst.*, 32, T109 (1941).
[29] Yackel, E C., and Kenyon, W. O., *J. Am. Chem. Soc.*, 64, 121 (1942).
Unruh, C. C., and Kenyon, W. O., *ibid.*, 127.

vestigated. It was found that, in the presence of water, the reducing type of oxycellulose is the principal product, although a slight increase in methylene blue absorption occurs. This is attributed, as in the case of other oxidizing substances, to the formation of some carboxyl groups. The rate of oxycellulose formation by ozone is greatly inhibited by first acetylating the cellulose, while the effect of mercerization is the reverse; that is, oxycellulose formation is accelerated by pretreatment with alkali.

A number of oxidizing agents such as hydrogen peroxide and sodium chlorite appear to be much less drastic in their effect on cellulose and accordingly have found use in commercial bleaching processes. It has been claimed that the latter bleaches cotton goods without affecting oxycellulose formation.[30] In the acid region (*i.e.*, chlorous acid), it oxidizes the aldehyde groups of modified celluloses to carboxyl groups without producing any other change. Thus, a dialdehyde type of oxycellulose produced by the action of periodic acid may be converted to a corresponding dicarboxylic acid by treatment with chlorous acid.[25]

Finally, it should again be pointed out that, while the oxidation of cellulose by periodic acid is confined largely to the glycol group and that produced by nitrogen dioxide to the primary hydroxyl group of the glucose residue, other oxidizing agents are less specific and probably result in mixtures of the above reactions. This fact has seriously complicated attempts to elucidate the nature of the chemical reactions involved. Further advances in our understanding of the nature of the reactions of various oxidizing agents with cellulose will depend on a more accurate evaluation of the number, type, and location of the ketonic, aldehydic, or carboxylic acid groups which may be produced during oxycellulose formation.

Most oxidized celluloses undergo a striking change when they are treated with alkaline solutions. It is possible to completely remove the reducing groups by such a treatment to the extent that the remaining cellulose cannot be distinguished in this respect from unmodified cellulose. This may or may not be accompanied by an appreciable loss in weight, depending upon the type of oxidized cellulose in question. The effect of the so-called "alkali boil" on oxycelluloses has been demonstrated by many investigators. The effect on nitrocellulose fluidity is shown by a comparison of the results in Figures 9 and 10. In addition to a change in this property, a loss in strength occurs because of the scission of alkali-labile linkages, and the production of short chain fragments.

The periodic acid oxycelluloses are particularly characterized by their susceptibility to further attack by alkaline solutions. The alkali-sensitivity of these materials, as measured by solubility in hot dilute sodium hydroxide and by cuprammonium fluidity is about proportional to the

[30] Vincent, G. P., *et al.*, *Am. Dyestuff Reptr.*, 30, 358 (1941).

content of aldehyde groups, at least in celluloses oxidized up to the extent of two glucose units in every hundred. It is of extreme interest that this sensitivity toward alkali is almost completely removed when the aldehyde groups are further oxidized to carboxyl groups [25] (by chlorous acid treatment). This same stabilization may be produced by the action of diazomethane on the periodate oxycellulose.[31] Thus, the sensitivity of this type of oxidized cellulose does not depend solely on the rupture of the glucose ring between carbon atoms 2 and 3, but is related to the specific instability towards alkali of the dialdehyde formed during the oxidation.

The efficacy of alkaline solutions in producing further degradation of oxycelluloses is apparently not dependent solely on hydroxyl-ion concentrations. A comparison of the effects on the nitrocellulose fluidity of modified cellulose after treatment with sodium hydroxide and with cuprammonium hydroxide solutions of approximately the same hydroxyl-ion concentration showed that the former had a greater effect on an acid hypochlorite oxycellulose, while the latter had a greater effect on other types such as dichromate-oxalic acid oxycelluloses. The effects of other basic compounds, such as Triton F (dibenzyldimethylammonium hydroxide), Triton B (benzyltrimethylammonium hydroxide), and cupriethylenediamine (all of which have been used for fluidity determinations), on the fluidity characteristics of modified celluloses have also been investigated. The degrading action of Triton F on alkali-sensitive modified celluloses appears to be similar to that of the inorganic alkalies. The fluidity in this solvent, unlike that in cuprammonium, is said to be a measure of the total chemical deterioration of the cellulose; that is, the solvent completely ruptures all alkali-labile linkages.

Although oxycellulose formation is in many cases accompanied by a decrease in the strength of the fibrous cellulose, the use of strength measurements as a measure of extent of oxidation may be misleading. This follows from the above discussion of the action of specific oxidizing agents in which it was pointed out that reducing oxycelluloses, such as those produced by periodic acid, may show little if any loss in strength although an appreciable amount of oxidation has occurred.

Acidic oxycelluloses, such as those produced by alkaline hypochlorite or by nitrogen dioxide, also vary in properties depending on the oxidizing agents and the conditions of oxidation. Nitrogen dioxide oxycelluloses which have carboxyl contents of 13% and above (theoretical for complete oxidation of primary alcoholic groups = 25.5%) are completely soluble in dilute aqueous solutions of sodium hydroxide, ammonia, sodium carbonate, and pyridine. The soluble salts formed with these bases may be precipitated by alcohol or other water-miscible nonsolvents. With polyvalent ions such as barium, insoluble salts are formed. The copper

[31] Reeves, R. E., *Ind. Eng. Chem. Ind. Ed.*, 35, 1218 (1943).

numbers of these oxycelluloses, which presumably should be low, are in-
deed very high; a sample which is completely oxidized gives a value whic
is theoretical for anhydroglucuronic acid calculated on the basis of th
reducing power of one aldehyde group for each uronic acid residue. Thes
results, as well as those obtained with incompletely oxidized materials, in
dicate that the copper number has no significance in respect to the oxycel
luloses of this type, but rather that reducing groups are formed durin
degradation in the alkaline copper solutions used in the copper numbe
method. That the carboxyl groups produced in oxidation of cellulose b
nitrogen dioxide are of the uronic type is shown by the quantitative evo
lution of carbon dioxide when the material is boiled in hydrochloric acid
Of interest in this connection is the fact that the carboxyl groups pro
duced by the action of chlorous acid on dialdehyde oxycellulose are no
decarboxylated by boiling hydrochloric acid. Thus, a method for th
partial allocation of carboxyl groups to their position in the glucos
residues of oxidized celluloses is available.[82]

## 3. Effect of Heat on Cellulose

The difficulties involved in establishing the course of the chemica
degradation of cellulose by heat are emphasized by the lack of specifi
information on the subject. Work has largely been limited to discussion
of the properties of celluloses degraded by this means. As in the instance
of other agents which produce degradation, the rate of breakdown is a
function of a number of possible variables. Perhaps the greatest single
factor influencing the extent of damage under a given set of conditions
is the duration of heating. Thus, prolonged exposure at low temperatures
may have a greater effect than exposure at high temperatures for shorter
periods of time. The magnitude of the effect may be judged by the loss
in breaking strength, rise in fluidity, increase in content of reducing
groups, and increase in solubility in alkali.

The first noticeable result of the effect of heat on cellulosic materials
is the loss of water. Below temperatures of 140° C. and a total time of
heating of four hours no great changes appear to occur.[83] Some recent
work,[84] however, has shown relatively small but measurable increases in
solubility in alkali and copper number at lower temperatures during short
intervals of heating.

The degradation is slower in the absence of oxygen, which indicates
that the initial stages of breakdown, at least, include oxidative destruction.

[82] Rutherford, H. A., Minor, F. W., and Harris, M. In preparation for publication.
[83] Doree, C., "The Methods of Cellulose Chemistry." D. Van Nostrand Co. (1933).
[84] Haas, H., *Kunstseide und Zellwolle*, 21, 88 (1939); Lewis, H. F., *Paper Trade J.*, 95, 29 (1932).

Continued heating, however, even in the absence of oxygen, leads to deterioration of the cellulose.

Stamm and Hansen[85] have postulated the formation of ether cross linkages to explain the decrease in affinity for water and in the ability to swell brought about by heating. While this hypothesis appears to explain a number of properties of celluloses after exposure to heat, there is no chemical evidence at hand to support the suggestion.

Other factors which influence the rate of tendering by heat are initial moisture content of the cellulose and of the surrounding atmosphere, the presence of impurities and the extent of pre-modification with respect to both hydrolysis and oxidation. Most regenerated celluloses, which have a low average chain length as compared with native cellulose, show rapid loss in strength under the influence of heat.

In a recent study of effects of drying conditions on the properties of textile yarns, it was shown that the "quality index" (defined as the percentage of the original breaking strength retained after drying multiplied by the percentage of the original elongation retained after drying) of cellulosic fibers decreases either as the temperature is increased or as the moisture content of the surrounding atmosphere is increased. The deterioration as measured by the fluidity method is shown in Figure 11. Both the breaking strength and fluidity of the purified cotton and the viscose rayon (Figure 12) appear to be functions of the relative humidity at which the samples are exposed. The damage is greater at a high humidity. In addition to a greater stability toward heat, cellulose acetate does not show the moisture sensitivity exhibited by the other two cellulosic materials.

It is apparent in the foregoing pages that the normal reactions of cellulose, occurring at or near room temperature, are directly related to the complex configurations of the cellulose molecule A great deal is known about the nature and kinetics of these reactions In contrast, at moderately elevated temperatures, the reactions of cellulose are appreciably more obscure and much less experimental data is available for verification of theoretical considerations. Finally, in the range of temperatures approaching that of a flaming fabric, the theoretical aspects of the degradation reactions become almost hopelessly complex and any truly fundamental consideration of mechanisms must rely on the simpler chemical reactions as discussed in the preceding section. A thorough understanding of these relationships will enable at least a partial extrapolation into the range of temperatures dealt with in the pyrolysis and combustion experiments which follow.

[85] Stamm, A. J., and Hansen, L. A., *Ind. Eng. Chem.*, 29, 831 (1937).

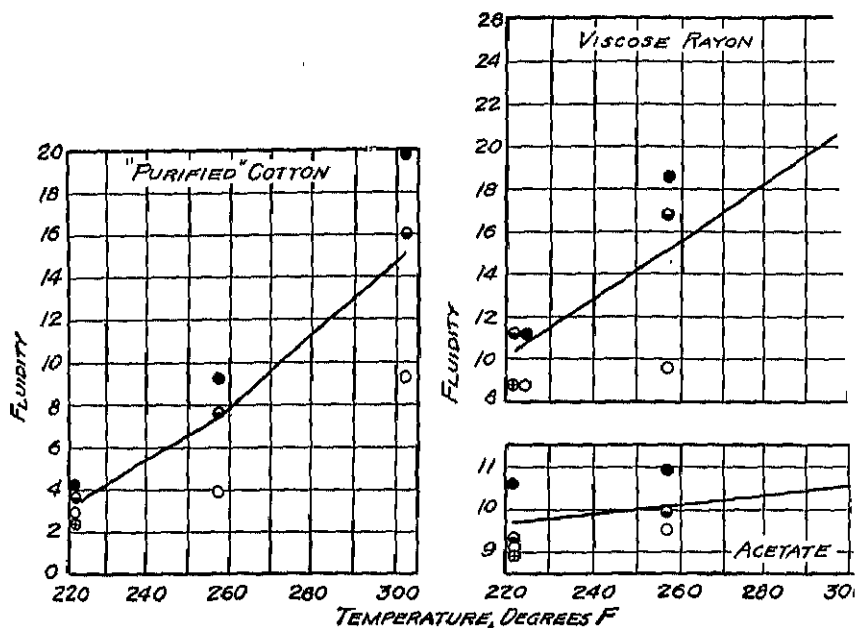



Figure 11. Effect of heat on the fluidity of yarns at low (○), medium (◒), a high (●) humidities; ⊕ represents initial fluidity. (*Wiegerink*[30])

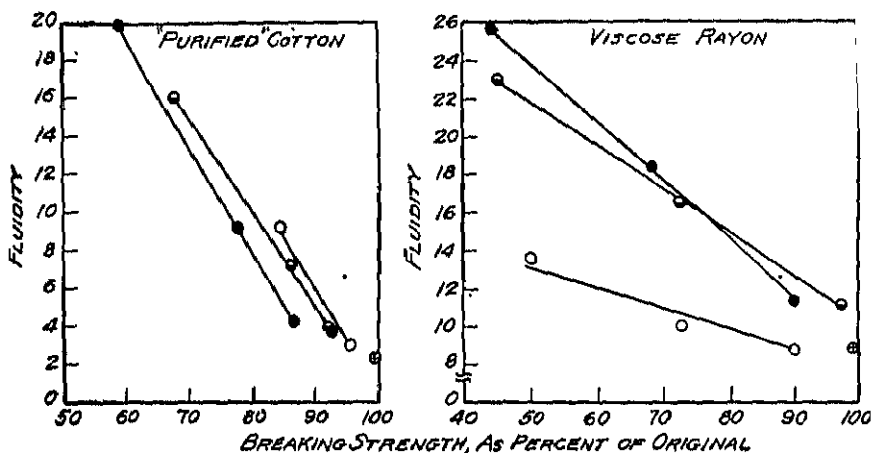



Figure 12. Relationship between fluidity and breaking strength of yarns which have been dried at low (○), medium (◒), and high (●) humidities; ⊕ represents initial relationship. (*Wiegerink*[30])

[30] Wiegerink, J. G., *J. Research Natl. Bur. Standards*, 25, 435 (1940).

## C. PYROLYSIS REACTIONS

*S. Coppick*

When cellulosic materials are heated at high temperatures in the absence of air, a rapid, typically pyrolytic reaction ensues. At least two additional phases are added to the system, which finally consists of a solid char, a liquid distillate, and a gaseous fraction. As would be expected, the rates of formation and ratios of the various product-phases depend to a great extent upon the conditions of the experiment and the precautions taken to isolate the initial products from the reaction mixture as soon as they are formed. Failure in rapid isolation and separation of these phases results principally in further cracking of some of the liquids to give additional amounts of solid and gases. In researches designed to determine the path of the primary breakdown of the cellulose molecule, it is therefore advisable to consider quite carefully the conditions under which the pyrolysis is performed.

Although pyrolytic disintegration proceeds quite freely by exclusion of the air via an inert gas such as nitrogen or carbon dioxide, it is preferable to carry out the decomposition at reduced pressure to facilitate the distillation of the high molecular weight products. The most readily adaptable and simplest approach is then by means of vacuum distillation in a closed system. Adaption of the principles of molecular distillation also aid in the isolation of the primary products of the reaction, and is readily accomplished by a condensing surface of high capacity as close as possible to the surface of the pyrolytic charge. The use of downward distillation rather than the normal, where some refluxing always occurs, is additionally favorable to removal of primary dissociation products from the ensuing reaction.

Adaption of these principles to a simple workable apparatus is demonstrated in the following design shown in Figure 13 Its efficiency is comparatively high, since yields of from 70 to 80% of liquid phases may be obtained from pure cellulose. This aqueous distillate contains the tarry products which are isolated by drying at 105° C., several hours being sufficient to attain a constant weight which is not appreciably affected by further drying for periods as long as 36 hours. Purified cotton normally yields about 50 to 55% of the dried tar. This material is easily removed by solution in methanol to facilitate determination of the char yield, the wet gas being determined by difference from the original charge in the bulb.

The effect of temperature on the pyrolysis of cotton is likewise followed most conveniently by observance of tar yields. When the initial absolute pressure in the system is of the order of magnitude of about 20

millimeters of mercury, and the temperature is increased above the cc lulosic decomposition point, the reaction becomes more and more rap until above 400° C. a constant rate is approached. This reaction velocit is observed as the rate at which the pressure change occurs in the systen The production of tarry products also increases with increasing tempera

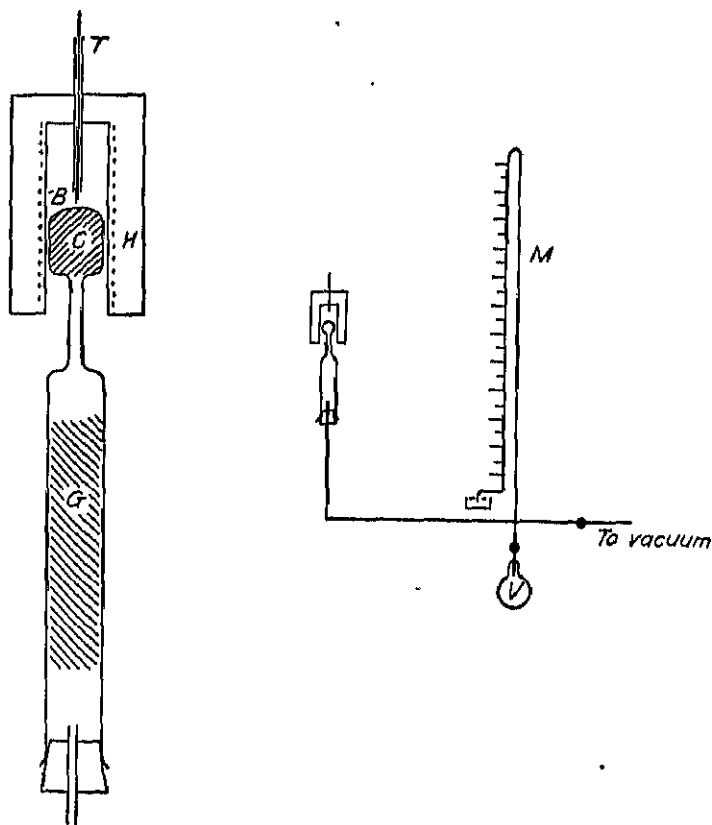



Figure 13. Equipment for pyrolytic investigations of the influence of retardants on the thermal decomposition of cellulose.

*T:* thermocouple; *B:* bulb from 1 by 8 inch test tube; *H:* heater; *C:* cotton; *G:* fiber-glass; *M:* manometer; *V:* volume of 500 cc.

ture, the dried yields at various temperatures being: at 300°, 33%; at 350°, 48%; at 400°, 52%; at 450°, 52%; and at 500°, 50%. Since burning fabric has been shown to attain a temperature in the vicinity of 500° C., and since the pyrolytic degradation appears to proceed at a constant rate in this range, it would seem that these conditions are admirably suitable for studies relating to the initial stages of the flaming decomposition reaction.

The absolute pressure in the system would be expected to exert several directing influences on the pyrolysis, higher pressures inducing further cracking of the tarry products as well as favoring their secondary oxidation. At 500° C. it is observed that as the initial absolute pressure is decreased below 600 millimeters of mercury, the tar yield is increased slowly from 40% until at starting pressures of 20 millimeters the yield has increased to 52%, which is not appreciably increased by additional reductions of the initial pressure.

Under these latter conditions, the last independent variable, pyrolysis time, is not critical. During the first two minutes of heating an induction period is observed which is associated with the thermal conduction of the system, as indicated by its dependence upon the initiating temperature. For the next two minutes the reaction proceeds very rapidly with the evolution of tarry and gaseous products, and is essentially complete at the end of the fifth minute, the pressure in the system rising only very slowly until about the tenth or fifteenth minute where it becomes practically constant. Hence, the conditions of 500° C., 20 mm. of mercury and 15 minutes of pyrolysis time are ideal for comparative studies.

When a number of the well-known soluble salts which are effective as fire retardants are added to cotton, certain well-defined changes are observed in both the rate and course of the pyrolysis. The induction heating period is decreased with increasing addition of the salt, probably by increased thermal conductance, and the velocity of the gas production is increased appreciably by the addition of small amounts of these salts. However, after the addition of about 10% of the retardants, the rate and quantity of gas evolution becomes practically constant at about twice its original value, as indicated by the rate and amount of mercury fall in the manometric system. Moreover, it is not only the effective flame retardants that exhibited this effect, for almost identical behavior is observed for inert materials such as sodium and potassium chloride which have little or no effect on the flaming characteristics of cellulose. It would appear that this ability of salts to increase both the rate and quantity of the gas phase resulting from the primary disintegration of cellulose is not specific for flame-retarding materials, but is a general phenomenon probably associated with a secondary independent reaction.

The other two pyrolysis phases, however, bear a more direct relationship to the flame-retarding properties of the salts. With the addition to cellulose of as little as 5% of a typical retardant such as diammonium phosphate, the tarry distillates are reduced in yield from about 55% to approximately 5% of the weight of the original cotton. On the other hand, a similar addition of an inert or poorly effective material such as sodium chloride only results in the reduction of the tarry products to a yield of about 30%. The ability to effect large decreases in the production of these tarry primary disintegration products appears to be specific for fire-

retarding materials. The sulfamates, sulfates and phosphates as their ammonium salts as well as the effective borax-boric acid mixture exhibit various efficiencies as depicted in Figure 14. In some cases, however, par-

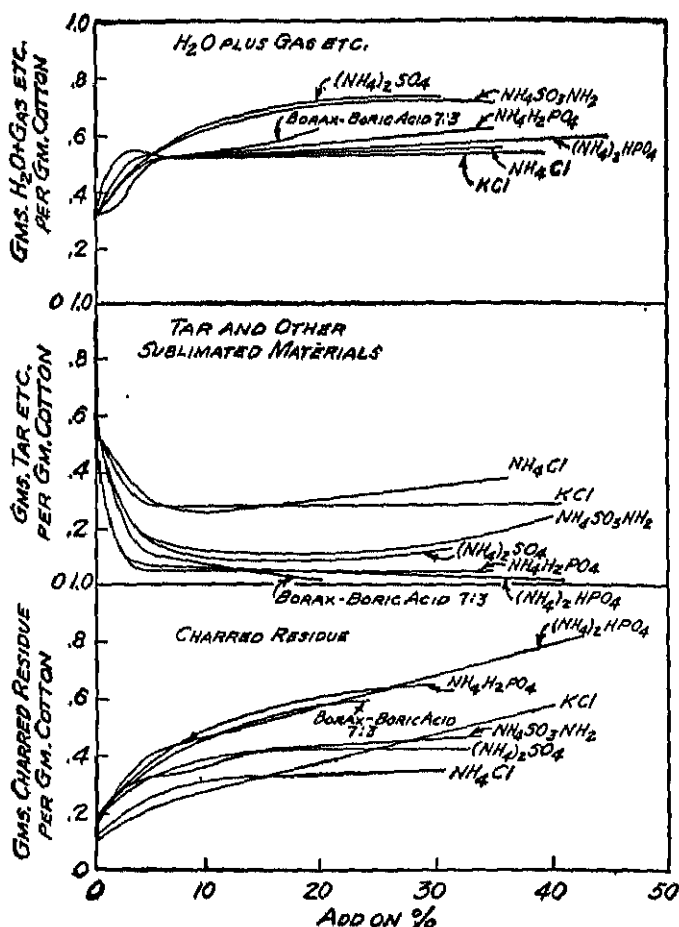



Figure 14. The influence of retardants on the quantity of the various phases resulting from the pyrolysis of cotton.

ticularly with the sulfamates, a true picture of the effectiveness cannot be obtained since the retardant itself decomposes and sublimes rather readily, and the tarry distillation products are contaminated with this sublimate. The maximum efficiencies of the various salts in tar-reducing capacity occur for the addition of the first 5 to 10% of material added to cotton, further additions having little or no subsequent effect. This is a particularly interesting behavior since it is well known that with the addition of these magnitudes of the effective retardants to a fabric, flame

propagation suddenly ceases and the amount of salt required for this protection is rather critical.

The amount of the third and last phase produced during pyrolysis, *i.e.*, the charred residue, likewise serves as a criterion of the flame-retarding efficiencies of various salts. The effective materials greatly increase the quantity of this char for small additions of the retardant. For instance the addition of 5% of the borax-boric acid mixture results in a char yield increase from the normal 10% to about 40%, while the ineffective potassium chloride increases the char yield only to 20% by a similar 5% addition of the salt. It is to be remembered here that the charred residue consists not only of the products from the cotton, but also of those from the retardant. In most cases these may be separated by hot water extraction of the residues, to leave a true char from the cellulose. In the case cited above, extraction shows that the true char from cotton treated with potassium chloride never exceeds a yield of 14% while that from the borax-boric acid mixture on cotton rises rapidly to 35% for less than 10% addition of the salts and finally becomes approximately constant in the neighborhood of 40% yield irrespective of the amount of retardant added to the cellulose.

In similar pyrolytic experiments on cotton fabrics it is observed that the tar production of the untreated material, although high, is not quite as great as that obtained with the absorbent cotton used entirely in the above. For the fabric, tar yields rarely exceed 42%, and depend somewhat upon whether the yardage is in the grey, desized, or dyed state These effects parallel to some extent actual inflammability as measured by flame propagation rates in the various fabrics and with absorbent cotton.

Commercially treated fabrics with good flame-retarding properties behave very similarly to the experimentally flame-proofed absorbent cotton The pyrolytic tars are low in yield and usually constitute from 5 to 10% of the original cellulose content of the material. The relative flame protection afforded by these treatments, as determined by practical flame tests, is nearly always in accord with their low tar-producing capacity. However, in a number of cases contamination of the tar renders its accurate determination difficult or impossible. This is particularly the case with treatments of the antimony oxide-chlorinated compound type, where sublimation of both constituents along with the tars takes place to such an extent that an apparent tar value of 27% is obtained for the fabric. This is certainly inconsistent with its performance.

From the above it may be concluded that the primary effect of flame-retarding chemicals is to alter the products resulting from the initial thermal decomposition of the cellulose molecule. The greatest change occurs in the solid and liquid phases, the gas being augmented in quantity somewhat both by retardants and nonretardants. However, the magnitude

of the changes of tar and char products is directly related to the fla proofing efficiency of the added salt. It has been observed further that tarry products are of a highly inflammable nature, are readily igni and propagate a flame very rapidly when impregnated on glass-wool asbestos fabric. It would appear then that these are the products m directly responsible for the flaming of cotton fabrics and that the m function of a retardant is to limit the production of these materials wl the fabric is subjected to a flame source.

The over-all effect of the efficient retardants appears to be the dir tion of the initial disintegration toward products in the solid phase ratl than along the lines of the normal and partial decomposition tow liquid phase fragments which vaporize, and on admixture with the oxyg of the air are readily ignited and constitute the flame. The prime ca for these effects is not considered here, but is postponed and will appe in the section devoted to the theoretical concepts postulated to explain t underlying principles involved in retardant action. All that is intend here is to delve as deeply as possible into the decomposition reactions an effort to bring to light conclusively the primary effects of retardan on cellulose at high temperatures.

## D. COMBUSTION REACTIONS

*S. Coppick*

The burning of organic materials in general is a very complex process involving a great number of steps wherein the material undergoes suc cessively many stages of disintegration and oxidation. A study of the fin end products leads to very little information regarding the intermediate which pass rapidly toward the lower energy levels and in the limit appea as carbon dioxide and water. It is of course well known that the efficiency of the process is directly concerned with the rate of oxygen supply and it concentration at the combustion source, which determine the extent o the energy drop in the final stages of the series of reactions. Thus, nor mally, the combustion of cellulose results in the formation of carbon monoxide as well as carbon dioxide and water. Smaller quantities of hydrocarbons such as methane sometimes occur but only under very adverse combustion conditions. Hence, investigations of the effect of retardants on the completed reaction are unprofitable, the products being practically identical for both treated and untreated cellulose and critically dependent upon the conditions of the oxidation. The only differences appear to be in the rate of the process as measured by the velocity at which a flame propagates throughout the mass of the material, and the extent to which the transfer from solid to gas phases occurs. This is measured very readily as the yield of residue remaining after ignition.

When flame propagation rates are reduced to zero by the application of an efficient retardant an impasse is reached, since it is here desirable to study a reaction which normally does not proceed. The approach must then be directed toward forcing the reaction in order to elucidate its normal inhibition. Moreover, during the thermal oxidation of cellulose three general reaction phenomena are observed, both the rate and extent of which depend not only upon the amount of the retardant added but also upon its nature. These are first, the propagation or chain reaction by which the incandescent gas meniscus is transported from one point to another. This reaction proceeds at velocities dependent upon a number of factors which include the state of division of the cellulose, the amount of retardant added, and the conditions of the experiment including the direction in which the flame travels. During horizontal flame propagation along a fabric, a deceleration is observed, while for vertical travel the velocity is greatly accelerated. Practically constant rates occur at angular directions in the neighborhood of from 30 to 45° to the horizontal.

As flame velocities are reduced by successive additions of an efficient retardant a critical point is usually reached at which the rate becomes zero. Here one enters the range of the forced reaction which is the second phase of flameproofing and involves the rate and extent of thermal decomposition of cellulose while in the presence of an instigating flame source. On removal of this source, provided the fabric has been efficiently treated, no chain reaction proceeds, although the flaming fabric may augment the source while the latter is present. This is the action which is finally observed as char length or area in practical flame tests or as the weight loss due to the decomposition.

The third and last general reaction phenomenon observed in the thermal oxidation of cellulose is the secondary exothermic decomposition of the solid products produced by either of the other two reactions This is the flameless combustion of the char identified as afterglow, and appears to be entirely independent of the flaming reaction, since it may be produced or eliminated at will by judicious choice of both the quantity and type of retardant employed

To further elucidate the primary effects which retardants have on the thermal oxidation of cellulose, it is advisable that the reaction be quenched during its preliminary stages for reasons similar to those stated in the previous section. The stipulation that the fragmentary decomposition products should be removed rapidly from the heat source appears to be even more critical when oxygen is present in the system. The arrangement of Figure 15 is adequate and is similar in principle to that previously used in vacuum studies, with the exception that the upper end of the tube is open to the atmosphere. Cellulosic material is placed in the upper bulb of the tube which is then inserted in the heater. The air drawn into the system via the aspirator is preheated on passage between the combustion

tube and the internal surface of the heater, and proceeding downw through the cellulose sweeps the fragmentary disintegration product

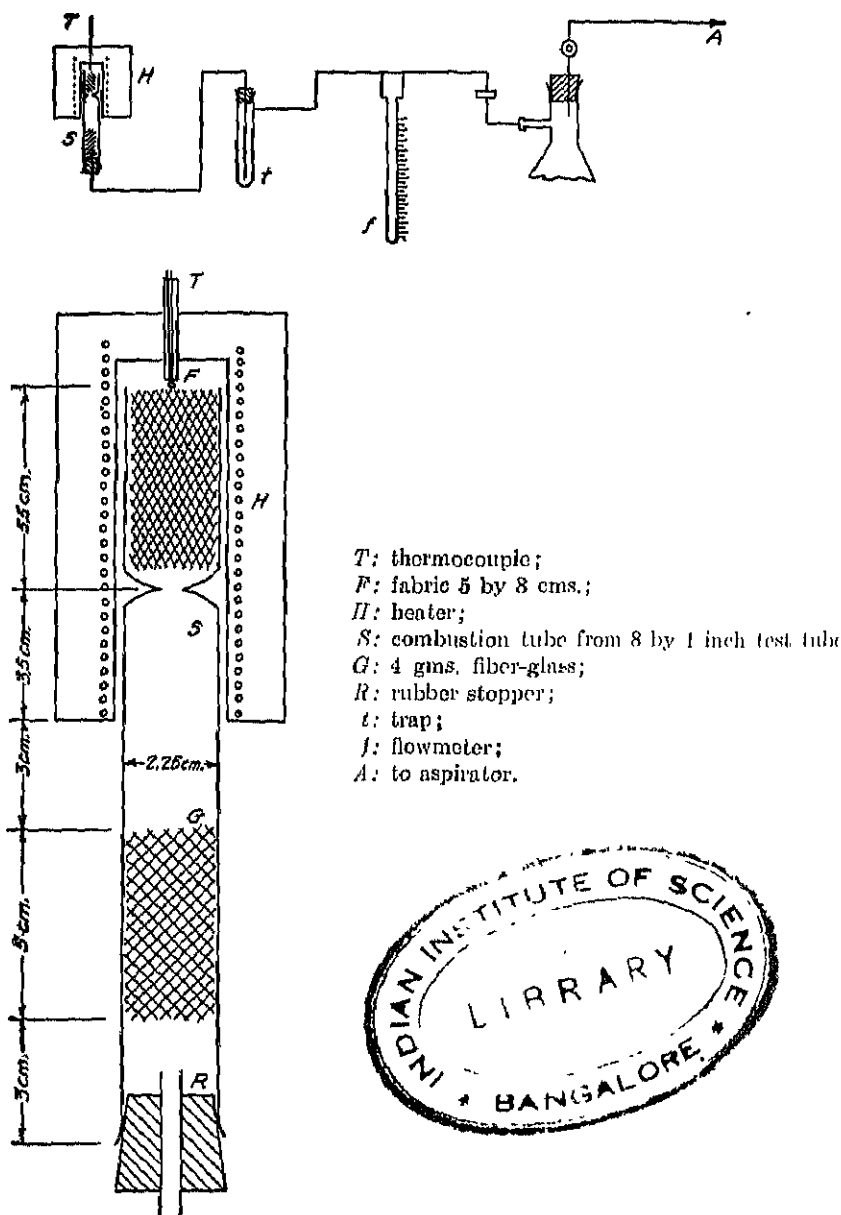
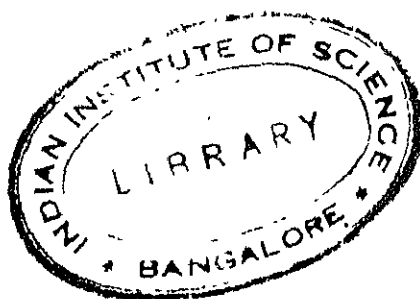



Figure 15. Equipment for controlled combustion investigations of the influence of retardants on the thermal decomposition of cellulose.

the large surface of the fiberglass condenser where they are absorbed. The determination of the various combustion phases is carried out as be-

fore. Cessation of the combustion at various intervals of time is accomplished by removing the tube from the heater and cutting off the air supply by inserting an asbestos stopper in the upper end of the combustion bulb.

Preliminary studies on absorbent cotton show that the rate of air flow is a rather critical factor in determining the ratio of the various phases formed at 500° C. Velocities such that less than 40 cc. of air per minute pass through the system are insufficient to give the liquid decomposition products the required directional influence to permit their accurate analysis, and their secondary cracking to solid and gas phases is indicated by the increased quantities of these products. Increasing the air flow from zero to 40 cc. per minute results in a dried tar yield increase from 9 to 40% of the original cotton. This yield is not changed by further increasing the air flow. However, the oxygen input represented by the rate of 40 cc. of air per minute is insufficient to promote a conveniently measurable rate for the secondary oxidation of the charred residue, which still retains a yield of about 10% even after 15 minutes of combustion at 500° C. Under these conditions the oxidation rate is gradually increased with increasing air input until at about 100 cc. per minute combustion of the char is complete in 15 minutes. To insure inclusion of an adequate safety factor it is preferable to carry out the oxidation at air input values considerably in excess of this minimum, and 180 cc. per minute appears to be satisfactory for differentiation purposes in a large number of treated and untreated cottons. The following experiments adopt these standard conditions For comparative determination of the flaming tendencies of fabrics it is convenient to use a propagation rate for those of easy ignition, while afterflaming and char dimensions characterize those whose propagation rate is reduced to a negligible value. These flame tests are described fully in a later chapter[37] devoted to testing procedures.

The influence of retardants on the products of the combustion of absorbent cotton is very similar to that found for the decomposition in vacuo. With addition of the well-known and effective salts such as the borax-boric acid mixture, the water-gas fraction is increased, the tarry products decreased and the charred residues increased The changes in the amounts of the various phases are again most pronounced in the region of the addition of up to 5 to 10% of these salts, which is again in agreement with their known flame retardation performance. In the case of the ineffective salts such as potassium chloride, the gaseous products are increased to an extent equal to that observed for very effective materials, but the quantities of tar and char products are quite different.

A typical set of data is shown in Figure 16, where distinction is made between the water-soluble and insoluble constituents of both the charred residue and the tarry distillate. Flame retardants such as the borax-boric

[37] Chapter IV, Section B–2, Flame Tests

acid mixture, calcium chloride or ammonium molybdate demonstr
ability to reduce the inflammable tars from a normal yield valu
to less than 5% of the original cotton. On the other hand, the
poorly effective potassium chloride seems unable to effect a tar r

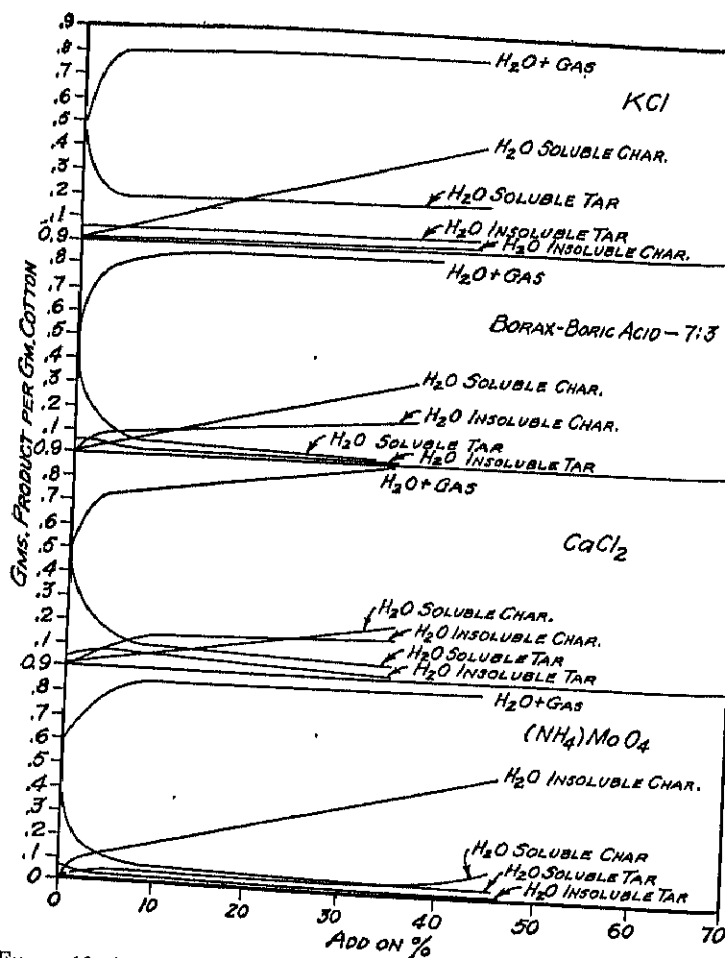



Figure 16. The influence of retardants on the quantity of the various phases resulting from the controlled combustion of cotton.

to less than 20% yield irrespective of the amount added to the fi
Similar effects are also observed with woven fabrics.

Some peculiar behavior is observed when either small amounts o
water-soluble retardants are added to cotton fabrics or when effecti
treated materials are leached with water until only slight traces o
original salts remain in the cell wall. It appears that these small amo
actually increase the velocity with which a flame will propagate along

fabric surface, although the addition of larger quantities reduces this rate, which in the limit becomes zero and the fabric is then substantially flameproofed. Investigations on the tar production in the range of increased inflammability show that although the amount of these volatile fragments is decreased slightly below the quantities obtained from untreated fabrics, these tars are more easily produced. Thus the effects of some retardants are competitive in nature, *i.e.*, a reduction in amount of fuel supply as tarry fragments but also an increase in their rate of generation at a given temperature. These opposing influences may either increase or decrease the tendency to propagate the flaming reaction and depend upon the concentration of the retardant in the fabric. Fortunately, however, the concentration coefficients for the extent and rate of the reactions are entirely different so that after the addition of more than 0.5% of these retardants the rate of tar production ceases to be the controlling factor and its lower quantity begins to exert a dominating influence which appears as a net reduction of the propagation velocity of the flame. These effects are shown in Table 2, which indicate the enhanced inflam-

Table 2. Effect of Small Amounts of Retardants on the Tar Production and Inflammability of Fabrics

| Retardant | Add-On % | No. of 15-min. Static Water Leachings | Tar mgs/cm² of Fabric | Flame Rate in/sec | Time to Maximum Tar Production min. |
|---|---|---|---|---|---|
| Ammonium | 0 | — | 11.88 | .103 | 4 |
| Dihydrogen | 0.05 | — | 9.92 | .161 | 3 |
| Phosphate | 0 1 | — | 9 12 | 218 | 2 |
| | 0.25 | — | 10.16 | .210 | 2 |
| | 0.5 | — | 6.68 | .137 | 2 |
| | 1 0 | — | 4 60 | .087 | 2 |
| Commercial | 0 | — | 11 88 | 119 | 4 |
| Sulfamate- | 0 5 | — | 10 15 | 197 | 4 |
| Phosphate | 0 1 | — | 10.37 | .203 | 3.5 |
| Mixture | 0 25 | — | 9 16 | .187 | 3 |
| | 0 5 | — | 6 75 | 153 | 3 |
| | 1.0 | — | 5 23 | .103 | 3 |
| Ammonium | 15 | 0 | — | 0 | — |
| Dihydrogen | | 1 | — | .105 | — |
| Phosphate | | 2 | — | 200 | — |
| | | 3 | — | 222 | — |
| | | 4 | — | .167 | — |
| | | 5 | — | .182 | — |
| Commercial | 15 | 0 | — | 0 | — |
| Sulfamate- | | 1 | — | .091 | — |
| Phosphate | | 2 | — | .222 | — |
| Mixture | | 3 | — | 200 | — |
| | | 4 | — | .208 | — |
| | | 5 | — | .143 | — |
| Desized Twill (untreated) | 0 | 0 | — | .133 | — |

mability induced by small amounts of either the phosphate or sulfa
type of retardants, whether traces of these salts are added directly o
the residual amounts remaining after the bulk of the retardant in an e
tively flameproofed fabric has been removed by leaching.

The increased addition of the effective salts to fabrics finally re
in a reduction of the inflammable tarry products below the thres
value required for self-sustaining of the flaming reaction and its prop
tion ceases. Further additions reduce the interval between removal of
instigating source and the cessation of the flaming reaction, until thi
turn reaches a zero limiting value. Still further addition of the retard
with its subsequent tar-reducing tendency promotes the reduction of fa
flaming even in the presence of the instigating source, which appears
the lessening of quantity or area of fabric destroyed by a flame of sta
ard aspect and duration, *i.e.*, a reduced char dimension. This very c
correlation between the flaming performance of fabrics and their
production capacity is apparent from Table 3, which includes data on
phosphate, sulfamate and borate types of retardants. It is seen that

Table 3. Correlation Between the Tarry Products from Controlled Combustion a the Burning Characteristics of Fabrics

| Fabric | Retardant | Add-On % | Tar from Combustion mgs/cm² of Fabric | Flame Rate in/sec | Vert After-flaming sec. | Ve Ch Len in |
|---|---|---|---|---|---|---|
| Desized Grey Goods | None | 0 | 15.2 | .164 | > 20 | 12 |
| Desized Twill (dyed) | " | 0 | 12.7 | .151 | > 20 | 12 |
| Regular Twill | " | 0 | 9.9 | .135 | > 20 | 12 |
| Grey Goods (sized) | " | 0 | 5.6 | .116 | > 20 | 12 |
| Desized Twill | Borax: | 0.2 | 8.6 | .111 | > 20 | 12 |
| | Boric Acid | 1.3 | 5.2 | .100 | 18 | 12 |
| | 7 : 3 | 1.6 | 4 3 | 069 | 19 | 12 |
| | " | 2.0 | 3.8 | .056 | 15 | 12 |
| | " | 3.5 | 2.5 | 0 | 7 | 5. |
| | " | 6.5 | 1 3 | 0 | 0 | 3. |
| | " | 13.6 | 1.1 | 0 | 0 | 2.1 |
| Desized Twill | Ammonium | 0.7 | 3.5 | .085 | > 20 | 12 |
| | Dihydrogen | 1.1 | 3.2 | .050 | > 20 | 12 |
| | Phosphate | 4.8 | 2.3 | 0 | > 20 | 12 |
| | " | 5.6 | 2.1 | 0 | 1 | 6 7 |
| | " | 8.2 | 2.3 | 0 | 0 | 5.7 |
| | " | 18.3 | 2.4 | 0 | 0 | 3.2 |
| Desized Twill | Commercial | 1.0 | 5.2 | .103 | > 20 | 12 |
| | Sulfamate- | 2.1 | 3.8 | .096 | > 20 | 12 |
| | Phosphate | 3.1 | 3.2 | 0 | > 20 | 12 |
| | Mixture | 5.1 | 2.8 | 0 | > 20 | 12 |
| | " | 9.6 | 2.2 | 0 | 0 | 3.9 |
| | " | 18.8 | 1.5 | 0 | 0 | 2.7 |
| | " | 31.2 | 1.0 | 0 | 0 | 2.7 |
| | " | 41.8 | 3.5 | 0 | 0 | 2.6 |

borax-boric acid mixture does not exhibit the behavior previously shown for the other two retardant types. The addition of 0.2% of this mixture gives no enhanced flame-spreading velocity such as demonstrated by the sulfamate-phosphate retardant mixture and by ammonium phosphate alone.

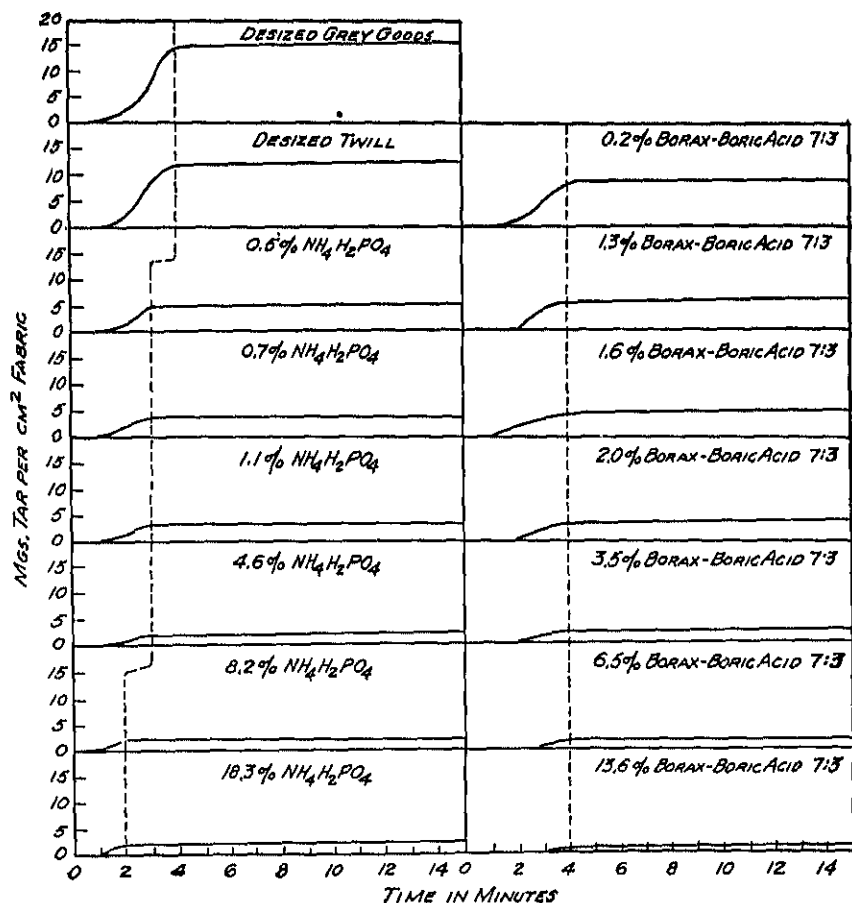



Figure 17. The effect of the phosphate and borate types of retardants on the rate of production of volatile cellulosic fragments during the controlled combustion of cotton fabrics. (The per cent values are those added to desized twill.)

The reason for this anomalous behavior becomes apparent from kinetic studies on the degradation reaction. Interruption of the combustion at successive time intervals of one minute over the whole of the 15-minute oxidation period and measurement of tar production leads to the determination of the rate of the process. It should be remembered, however, that the experiment is not conducted entirely isothermally since an

induction period is necessitated wherein the fabric is raised over a temperature gradient from room conditions to approximately 50 With an untreated fabric, tar production does not begin until aft first minute of exposure and proceeds at increasing velocity over th minute with increasing charring of the fabric. During the third minu is evolved at its maximum velocity which appears to be constant f material and independent of the initiating temperature. The slower c rate apparently is due to non-uniform attainment of the decompo temperature, and less rapid decompositions at intermediate tempera As the reaction approaches completion toward the fourth minute th of tar production decreases and at the end of the fourth minute the ar of tar reaches a constant value, which is not affected by further in ing the combustion duration up to 15 minutes.

The effect of both the phosphate and borate mixture is quite si as far as their influence on the quantities of the product are conce although the borate appears to have a greater efficiency in tar redu However, their effect on the temperature coefficient and rate of th action appears to be entirely different, as demonstrated in Figur With the phosphate retardant, the time interval over which tar is duced is reduced from three- to a one-minute period for successive tions up to 8% of the retardant and the reaction is then complete a end of the second minute. In the case of the borate retardant, o other hand, no change in the heating period required for completion o tar generation reaction is observed, an interval of 4 minutes bein quired irrespective of the amount of these salts added to the fabric. ilar rate differences are found for the decomposition of the solid p and it appears that the borate mixture has the advantage of not taining the two competitive factors of rate and extent of reaction, w render the phosphate a flame promoter in the low addition range. changes for tar production, similar to those depicted in Figure 17 fo phosphate, have been observed for the commercial sulfamate-phosp mixture, sulfamate alone, and permanently phosphated fabrics as as for the 7:3:5 mixture of borax, boric acid and ammonium phosp and appear to be associated with the strong acid type of retardant. C parative charring of the fabric during the early stages of the combus is seen in the photographs of Figure 18. These effects indicate that the types of retardant function via somewhat different mechanisms.

## E. THERMAL DECOMPOSITION PRODUCTS

*S. Coppick*

### 1. Gas Phase Products

In the previous sections devoted to the reactions ensuing during pyrolysis and controlled combustion of cellulose and its retardant c

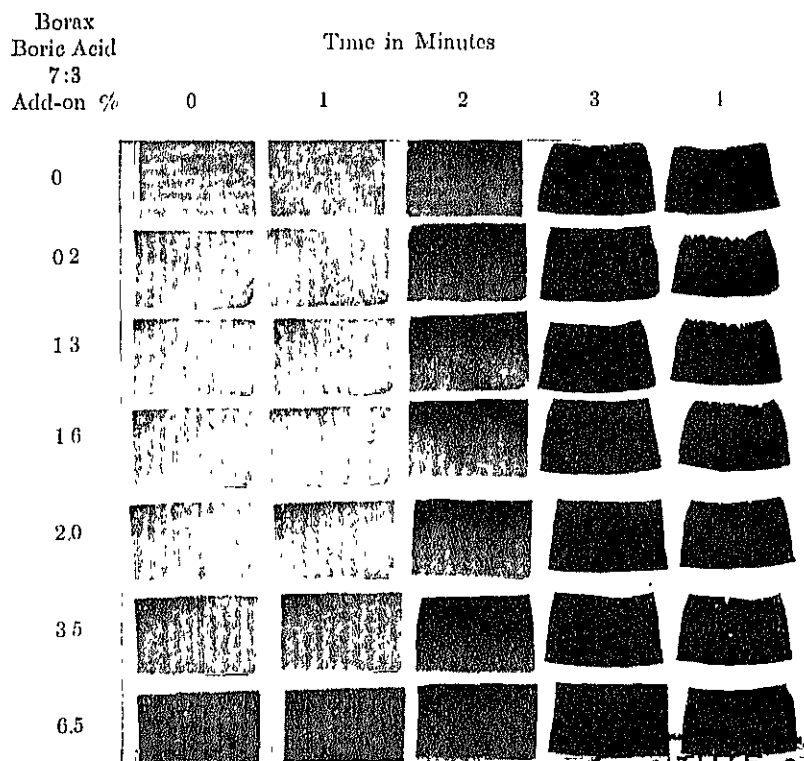
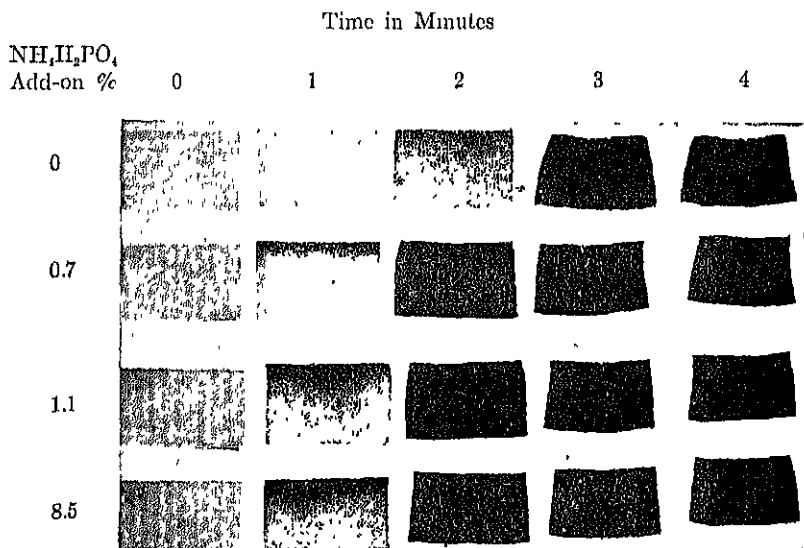



Figure 18. Comparative charring rates for the phosphate and borate types of retardants during controlled combustion.

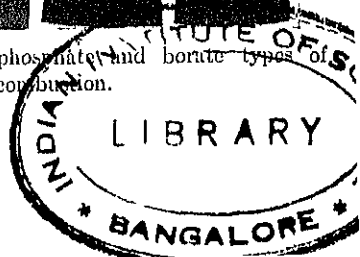
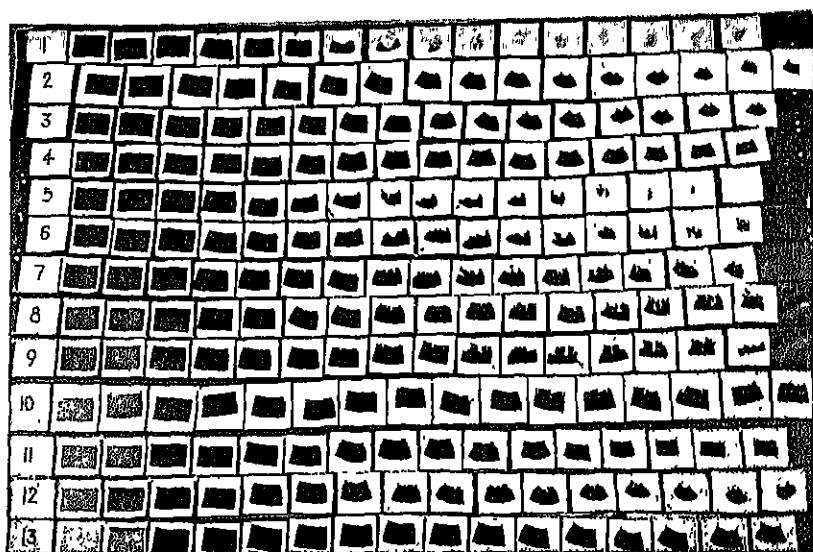



Figure 23. Charred residues at 1-minute intervals during the controlled combustion of fabrics.

1. Untreated
2. 0.7% Ammonium dihydrogen phosphate
3. 1.1% Ammonium dihydrogen phosphate
4. 8.5% Ammonium dihydrogen phosphate
5. 0.2% Borax:Boric acid::7:3
6. 1.3% Borax:Boric acid::7:3
7. 1.6% Borax:Boric acid::7:3
8. 2.0% Borax:Boric acid::7:3
9. 3.5% Borax:Boric acid::7:3
10. 6.5% Borax:Boric acid::7:3
11. 8.2% Borax:Boric acid:Ammonium dihydrogen phosphate::7:3:5
12. 8.5% Commercial sulfamate-phosphate mixture
13. 16% Commercial urea-phosphate type treatment

binations, it is seen that although the products in the gaseous phase are augmented both in amount and production rate, their values do not appear to be critically related to the flaming mechanism and its deceleration. Both retardants and non-retardants show very similar effects in enhancing the quantity of vapors and the velocity of their generation, but there still remains the possibility that the vapor composition might be variable.

It is to be remembered that in the previously described experiments the gas phase has always included the water produced in the decomposition. However, the determination of the dry gas phase is easily carried out by measurement of weight losses involved in experiments conducted via

Table 4. The Effect of Retardants on the Amount of Dry Gas Produced During the Pyrolysis of Fabrics
Treated with the Sulfamate-Phosphate Retardant System

| Retardant | Add-On % | Pressure Increase mm. of Mercury | Quantity of Gas % by Wt. | mgs/cm² of fabric |
|---|---|---|---|---|
| Ammonium | 0 | 87 | 1.8 | 0.46 |
| Dihydrogen | 0.5 | 214 | 6.0 | 1 52 |
| Phosphate | 1.3 | 250 | 6 1 | 1.56 |
| | 3.1 | 258 | 6.4 | 1 63 |
| | 6.6 | 308 | 17 6 | 4 45 |
| | 17.2 | 258 | 14.5 | 3.19 |
| Ammonium | 0 | 87 | 1.8 | 0 46 |
| Sulfamate | 3 5 | 234 | 6 9 | 1 56 |
| | 4.1 | 376 | 11.0 | 2 80 |
| | 8 1 | 374 | 12 5 | 2.88 |
| | 12 7 | 519 | 15.8 | 4 49 |
| | 25.1 | 464 | 13.1 | 3.88 |
| Commercial | 0 | 87 | 1 8 | 0 46 |
| Sulfamate- | 2.1 | 263 | 6 0 | 1.54 |
| Phosphate | 3.1 | 332 | 8 7 | 2 20 |
| Mixture | 5.1 | 380 | 8 6 | 2.54 |
| | 9.6 | 385 | 9 9 | 2 54 |

modification of the equipment of Figure 13. Replacement of the glass wool in the sorption section of the condenser by a dehydrating agent ensures collection of both tarry and aqueous distillates. The rate of the process is observed as usual by the rate of pressure increase in the system, and the extent of the reaction by the total pressure increase when equilibrium is attained. The results for various retardant types added to cotton fabrics are given in Table 4, wherein the quantities of dried gas show effects with increasing retardant addition similar to those previously discussed for the saturated gas phase. The rate at which this phase is produced is increased substantially by relatively small additions of effective flame decelerants of the borate, phosphate and sulfamate type. In the neighborhood of about 5 to 10% addition of these salts the quantity and production rate become practically constant and even appear to pass

through a maximum, further additions of the retardant causing a s
reduction in the amount of gas.

Great changes in the flame-retarding characteristics of fabrics ma
obtained by variations in a complex system involving the three con
nents, borax, boric acid and ammonium phosphate. Investigation of
dry gas from the pyrolysis of fabric treated with various amounts of
of these components and their mixtures produce the *results* giver
Table 5. It appears that the quantity augmentation of the dry gas phas

Table 5. Dry Gas Variations in the Pyrolysis of Fabric Treated with Borax, Boric
and Their Mixtures

| Retardant | Add-On % | Pressure Increase mm. of Mercury | Quantity of Gas % by Wt. | Quantity of Gas mgs/cm² of fabric | Vertic Afterfla sec |
|---|---|---|---|---|---|
| Boric Acid | 0 | 212 | 1.75 | 0.47 | > 2 |
| | 3.4 | 482 | 11.33 | 2.51 | > 2 |
| | 5.4 | 437 | 8.85 | 2.27 | > 2 |
| | 7.7 | 448 | 10.65 | 2.50 | > 2 |
| | 10.4 | 435 | 8.77 | 2.20 | > 2 |
| | 10.5 | 449 | 9.95 | 2.35 | > 2 |
| | 13.0 | 472 | 9.23 | 2.38 | > 2 |
| Borax | 0 | 212 | 1.8 | 0.46 | > 2 |
| | 2.8 | 388 | 10.2 | 2.59 | 15 |
| | 5.4 | 400 | 10.4 | 2.62 | 3 |
| | 12.9 | 427 | 10 7 | 2.99 | 3 |
| | 20.3 | 413 | 10.7 | 3.01 | 3 |
| | 29.0 | 417 | 10.3 | 3 15 | 3 |
| | 34.5 | 419 | 9.1 | 3.01 | 0 |
| Borax: Boric Acid 7 : 3 | 0 | 212 | 1.75 | 0.47 | > 20 |
| | 2.5 | 492 | 10.42 | 2.61 | 18 |
| | 4.6 | 534 | 10.25 | 2.89 | 0 |
| | 8.4 | 558 | 10.89 | 2 97 | 0 |
| | 16.5 | 538 | 9.20 | 2 58 | 0 |
| | 30.1 | 564 | 8 99 | 2.82 | 0 |
| | 43.7 | 608 | 9.35 | 3.21 | 0 |
| Borax: Boric Acid: Ammonium Dihydrogen Phosphate 7 : 3 : 5 | 0 | 212 | 1.75 | 0.47 | > 20 |
| | 3.9 | 540 | 10.49 | 2.67 | > 20 |
| | 5.6 | 482 | 8.75 | 2.37 | > 20 |
| | 10.4 | 495 | 8.77 | 2.45 | 0 |
| | 19.2 | 524 | 8.13 | 2.70 | 0 |
| | 34.2 | 420 | 6.86 | 2.31 | 0 |
| | 59.9 | 515 | 6.96 | 2.48 | 0 |

a general phenomenon and bears little if any relation to the flaming characteristics of the fabric since the ineffective boric acid produces effects almost identical with those given by equal additions of either the fairly effective borax, the good three-component or the excellent two-component retardant system. The vertical afterflaming values characterize the relative burning properties of the various treated fabrics.

For more complete characterization of the gaseous phase produced during the pyrolysis of treated and untreated fabrics, the vapors must be isolated and subjected to the standard analytical procedures. A convenient and satisfactory system is shown in Figure 19, where the pyrolysis is carried out in a small bulb (shown inside the heater) over an adjustable mercury column in the pipette, $B_1$. After completion of the reaction the heater is removed and the specimen bulb cooled. The sealed capillary point, $p_1$, is then connected to the analytical system at $P_2$ via rubber tubing, and by breaking the capillary the gases may be transferred to $B_2$,

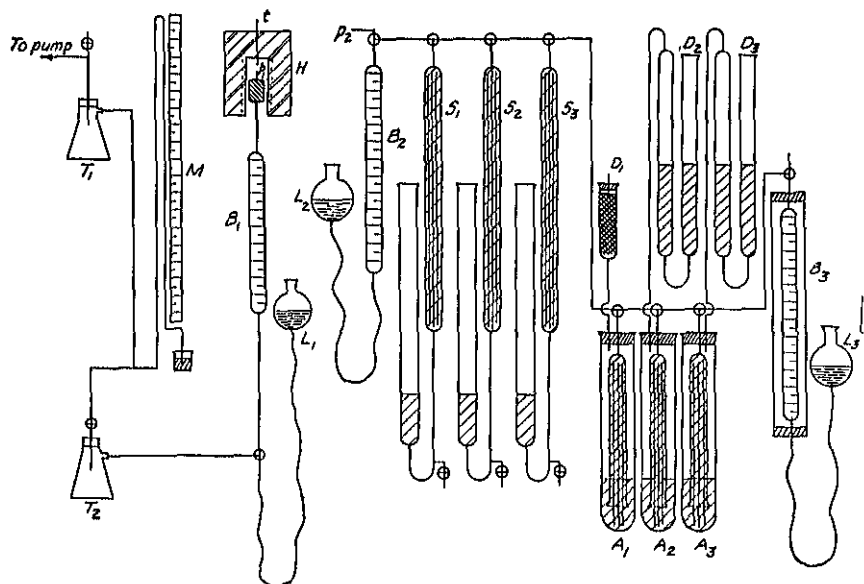



Figure 19 Equipment for the determination of the composition of the gas phase generated during the pyrolysis of cellulose in the presence of various retardants.

*M*: manometric system; $T_1$, $T_2$ traps; *H*: heater; *t*. thermocouple, $p_1$: sealed capillary on fabric bulb; $B_1$, $L_1$ gas collecting system, $B_2$, $L_2$: gas measuring system; $P_2$: connection to analytical system; $S_1$, $S_2$, $S_3$ gas scrubbers, $A_1$, $A_2$, $A_3$ gas absorbers; $D_1$: ascarite trap, $D_2$, $D_3$ water traps, $B_3$, $L_3$ Orsat burette system

where they are retained over mercury. The soluble constituents are determined by washing the gases in the three scrubbing sections, $S_1$, $S_2$ and $S_3$. On transfer to the burette, $B_3$, where the saturated gas is maintained over water, its constitution is determined by selective absorption in the standard Orsat bulbs at $A_1$, $A_2$ and $A_3$. The Ascarite trap, $D_1$, and water traps, $D_2$ and $D_3$, protect the absorption liquids in $A_1$, $A_2$ and $A_3$ from the outside atmosphere.

In the case of the controlled combustion of fabrics the products are identified by use of a modification of the equipment shown in Figure 15. The inclusion of U-tubes containing "Drierite" and "Ascarite" in series

with the tar absorber facilitates the determination of the aqueo
$CO_2$ constituents.

Investigation of the total pyrolytic gas phase resulting from t
composition of fabric treated with the commercial phosphate and
mate mixture indicates as usual an increase in the amounts produce
increasing addition of the retardant. This increase is not at all
with the add-on but assumes a maximum in the vicinity of a 10%
tion? Similar effects are observed for each of the constituents alo
plied to fabrics. Moreover, it is observed that the augmentation is n
entirely to vapors arising from the decomposition of the retardant
on scrubbing the gases from fabrics the same maxima occur, while
retardants are added to glass fiber the resulting vapors are all diss
in the scrubbing process. The effects appear to be associated wit
actual course of the decomposition of the cellulose itself, the reta
exerting more of a directing rather than a contributing effect to this p

The sulfamate-phosphate system does not lend itself very w
studies of this kind due to the complexity of the sulfur compo
evolved during the decomposition. A much simpler system from an an
ical point of view is found in the borate mixtures on which a ver
tailed investigation is shown by the data of Table 6, where the co
nents and mixtures of the retardant system are compared with so
chloride.

It appears that the pyrolytic gases show the same type of beh
previously demonstrated in the sulfamate-phosphate system, the retar
increasing the total quantity of this phase to about twice its normal v
These gases contain about 35% of readily soluble constituents whicl
very probably the lower molecular weight aldehydes and acids, 35%
15% hydrocarbons and about 15% $CO_2$, the latter being the only n
flammable constituent. With the addition of the retardants of var
flame-retarding efficiencies, the distribution of the quantities of the infl
mable constituents varies somewhat, but the non-flammable $CO_2$ c
stituent remains approximately constant. There appears to be no rad
difference in the over-all composition as one proceeds from the ineffec
sodium chloride and boric acid through the fairly effective borax to
very efficient 7:3 mixture. The general indication is that the gas pl
maintains approximately constant flammability composition but incre
in amount on the addition of any salt to the fabric.

Similar effects are observed in the data accumulated in combust
studies. Here, due to presence of air during the thermal decompositi
some of the flammable gases produced in the primary dissociation are f
ther oxidized to $CO_2$, thus this component increases with increased g
production. However, the amount arising from fabric treated with Na
is about the same as that from fabric treated with the effective retardan
The same appears to be true of the aqueous constituent which increas

Table 6. The Effect of Various Materials on the Composition of the Gases Evolved During the Pyrolysis of Cotton Fabrics

| Retardant | Add-On % | Total Gas cc/cm² of fabric | Gas Components (% by volume) H₂O Solubles aldehydes, acids, etc. | CO | Hydro-carbons, etc. | Total Inflam-mables | $CO_2$ |
|---|---|---|---|---|---|---|---|
| Sodium Chloride | 0 | 1.04 | 43.2 | 32.5 | 14.2 | 89.9 | 10.1 |
| | 3.1 | 3.67 | 35.8 | 30.8 | 18.6 | 85.2 | 14.8 |
| | 7.0 | 3.77 | 36.2 | 31.8 | 18.5 | 86.5 | 13.5 |
| | 13.5 | 1.96 | 35.3 | 32.5 | 18.1 | 85.9 | 14.1 |
| | 26.4 | 3.22 | 35.9 | 32.3 | 20.5 | 88.7 | 11 3 |
| | 33.7 | 2.45 | 38.7 | 25.0 | 21.4 | 85.1 | 14.9 |
| Boric Acid | 0 | 1.04 | 43.2 | 32.5 | 14.2 | 89.9 | 10.1 |
| | 3.5 | 1.50 | 34.6 | 41.0 | 14.5 | 90.1 | 9.9 |
| | 7.7 | 1.75 | 30.8 | 44.3 | 15.2 | 90.3 | 9.7 |
| | 10.5 | 1.81 | 31.4 | 46.0 | 13.0 | 90.4 | 9.6 |
| | 13.0 | 1.92 | 27.1 | 48.3 | 15.8 | 91.2 | 8.8 |
| Borax | 0 | 1.04 | 43.2 | 32 5 | 14 2 | 89.9 | 10.1 |
| | 2.8 | 2.41 | 29.0 | 36 4 | 15 6 | 81.0 | 19 0 |
| | 5.4 | 2.17 | 34.6 | 33 7 | 16.3 | 84.6 | 15.4 |
| | 13.0 | 2.25 | 34.6 | 36.2 | 13 1 | 83.9 | 16.1 |
| | 20.3 | 2.10 | 36 2 | 37 0 | 12 4 | 85 6 | 14.4 |
| | 29.0 | 2.15 | 40 0 | 27.0 | 18.0 | 85 0 | 15.0 |
| | 34.5 | 2.29 | 34.9 | 29 8 | 19 5 | 84 2 | 15.8 |
| Borax: Boric Acid 7 : 3 | 0 | 1.04 | 43 2 | 32 5 | 14.2 | 89 9 | 10.1 |
| | 2.6 | 2.03 | 39 5 | 33 5 | 16 9 | 89 9 | 10 1 |
| | 4.6 | 2.50 | 37.9 | 33.9 | 18 0 | 89.8 | 10 2 |
| | 8.4 | 2.30 | 38 6 | 37 9 | 12 7 | 89 2 | 10.8 |
| | 16.5 | 2.45 | 39 2 | 33 8 | 16 4 | 89 4 | 10 6 |
| | 30.1 | 2.54 | 36.9 | 36.4 | 13 9 | 87 2 | 12 8 |
| | 43 7 | 2.35 | 42 3 | 33 5 | 12 1 | 87 9 | 12.1 |

somewhat with addition of the salts, but is apparently the same for all, irrespective of their flameproofing action On this basis, there appears to be little if any justification for further consideration of the gas phase as being directly related to retardant action. However, the other volatile but readily condensable products, accumulated as tars, appear to be more closely related to non-flaming tendencies and are considered in detail in the following section.

## 2. Liquid Phase Products

The aqueous distillate obtained from the pyrolysis or controlled combustion investigations contains the tarry primary dissociation products which appear to be critically related to the flaming characteristic of fabrics. In the borate retardant system, the agreement between the flame test data and the dry tar is particularly good. This system lends itself very readily to studies of this kind since the retardant does not contaminate

the distillates, which may be determined with considerable accurac precision with which this phase follows the inflammability of treat ton fabrics is demonstrated in Figure 20, where large reduction amount is observed for mixtures of borax and boric acid when th ponents are in the ratio of 1:1 or 7:3. However, when the boric aci dominates in the system, as in the 3:7 mixture, the tar reduction quite as great, which corresponds to the poorer flame-retarding qu of this blend. Moreover, the individual components alone on the

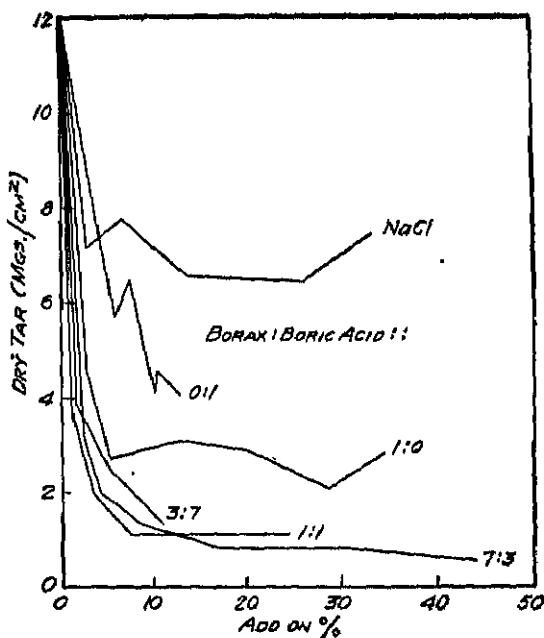



Figure 20. The red in the amount of cellulosic fragments as enced by mixtures of and boric acid in comp with that produced b dium chloride

follow the order of their fair to poor efficiencies compared with the i and ineffective sodium chloride. The relation between the tars and b ing characteristics is summarized in Figure 21 for this system, whe it seems that the production of these fragments must be reduced be 2 milligrams per square centimeter of fabric before flaming cease the vertical strip test immediately on removal of the flame source value appears to be rather critical, and increasing the tar yield fro to 4 milligrams per centimeter of fabric results in considerable flan after the instigating source has been removed, although propagatio the flame may not proceed longer than 10 or 20 seconds. However, v the fuel supply greater than 4 milligrams, continuous burning proce until the fabric is completely consumed.

The total condensable distillates resulting from the combustion exp ments contain considerable water. The aqueous portion is increased w the addition of salts to the fabric, while the tarry products are decrea

greatly for the addition of the effective retardants. The net result, as shown in Table 7, is not only a reduction in the amount of the tarry fuel supply but also a lowering of its effective concentration by dilution with water.

Although the supply, rate and concentration of these volatile fragments are altered radically by the effective retardants, their actual composition does not appear to be changed to any great extent. The tarry constituents contain hydroxyl, methylene, methyl, carbonyl, ethylene and ester groupings as determined by their infrared absorption spectra, which is in har-

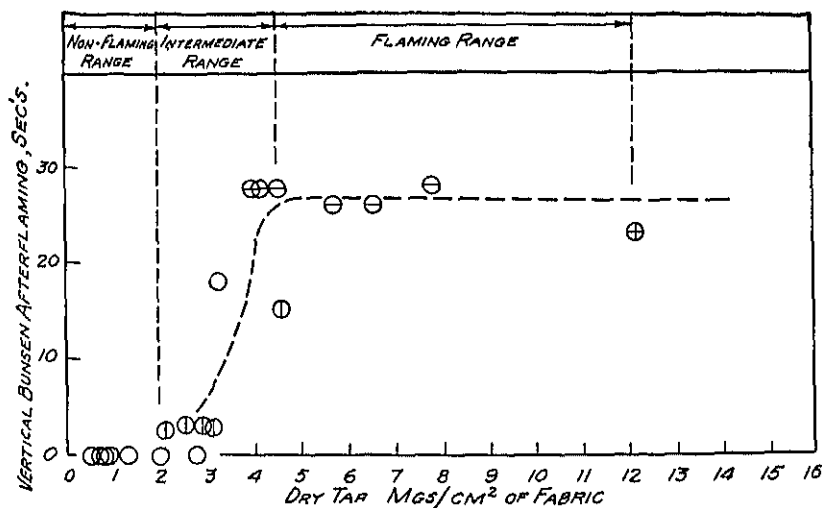



Figure 21. The correlation between the evolution of volatile fission products from cellulose and the flaming characteristics of fabrics.

⊕ untreated fabric, ⊖ treated with boric acid; ⦶ treated with borax, and ○ treated with borax and boric acid in the weight ratio of 7 3

mony with theoretical considerations regarding the probable course of the disintegration of the cellulose molecule. Moreover, the absorption curves of the tars from treated and untreated cotton show the same general absorption maxima and with nearly equal intensities

The analytical data suggest degradation nuclei of the pentose or furfural type, with composition not varying very widely with the amount of retardant or its type. As shown in Table 8, the carbon and hydrogen content of the various tars show no distinct variation with the effectiveness of the retardant, and although the products are highly reducing in nature their carbonyl content is not greatly changed by retardant additions.

Measurement of the relative inflammabilities of the tars from treated and untreated cotton indicates no great differences in the rates of flaming with different retardants. The conditions of burning fabric are readily

Table 7. The Variation of the Quantities of Liquid Phases Produced During trolled Combustion of Cotton Fabrics in the Presence of Various Materi.

| Retardant | Add-On % | Dry Tar mgs/cm² | Aqueous Fraction mgs/cm² | Tar in Distillate % | Af |
|---|---|---|---|---|---|
| Sodium Chloride | 0 | 12.20 | 9.24 | 56.9 | |
| | 3.1 | 7.05 | 14.31 | 33.0 | |
| | 7.0 | 7.80 | 10.25 | 43.2 | |
| | 13.5 | 6.50 | 13.88 | 31.0 | |
| | 26.4 | 6.43 | 14.37 | 30.9 | |
| | 33.7 | 7.48 | 14.02 | 34.8 | |
| Boric Acid | 0 | 12.20 | 0.24 | 56.0 | |
| | 3.5 | 7.86 | 15.90 | 33.1 | |
| | 7.7 | 6.53 | 15.65 | 29.4 | |
| | 10.5 | 4.52 | 15.03 | 23.1 | |
| | 12.0 | 4.00 | 14.15 | 22.0 | |
| Borax | 0 | 12.20 | 9.24 | 56.9 | |
| | 2.8 | 4.55 | 4.76 | 27.9 | |
| | 5.4 | 2.62 | 14.25 | 15.5 | |
| | 12.9 | 3.08 | 15.90 | 16.2 | |
| | 20.3 | 2.88 | 15.28 | 15.8 | |
| | 29.0 | 2.08 | 14.65 | 12.4 | |
| | 34.5 | 2.75 | 15.86 | 14.8 | |
| Borax: Boric Acid 7 : 3 | 0 | 12.20 | 9.24 | 56 9 | |
| | 2.6 | 3.18 | 12.57 | 20.2 | |
| | 4.6 | 1.97 | 13.26 | 12.9 | |
| | 8.4 | 1.28 | 13.90 | 8.4 | |
| | 16.4 | 0.85 | 12.48 | 6.4 | |
| | 30.1 | 0.83 | 14.49 | 5.4 | |
| | 43.7 | 0.55 | 10.10 | 5.2 | |

Table 8. The Properties of the Tarry Distillation Products Isolated During the trolled Combustion of Absorbent Cotton

| Retardant | Add-On % | C % | H % | Reducing Power CuO gms/gm tar | Fraction of Tar Dissolv in % Water | Acetone | Isopr |
|---|---|---|---|---|---|---|---|
| Sodium Chloride | 0 | 48.43 | 6.67 | 0.47 | — | — | – |
| | 1.1 | 51.66 | 6.35 | 0.43 | — | — | – |
| | 2.7 | 54.90 | 6.33 | 0.35 | — | — | – |
| | 7.0 | 53.51 | 6.47 | 0.40 | — | — | – |
| | 16.2 | 53.43 | 6.53 | 0.38 | — | — | – |
| Boric Acid | 0 | 48.43 | 6.67 | 0.47 | 13.6 | 45.5 | 36 |
| | 2.5 | 48.85 | 6 67 | 0.50 | 22.9 | 50.7 | 5 |
| | 3.5 | 49.17 | 6.18 | 0.50 | 16.1 | 45 7 | 23 |
| | 5.3 | 46.25 | 5.95 | 0.55 | 24.7 | 46.9 | 15 |
| | 7.3 | 42.10 | 6.37 | 0.49 | 40 2 | 43.6 | 26 |
| | 12.3 | 35.30 | 8.57 | 0.41 | 17.8 | 36.9 | 39 |
| | 21.6 | 25.69 | 7.88 | 0.42 | 23 2 | 29.0 | 34 |
| Diammonium Phosphate | 0 | 48.43 | 6.67 | 0.47 | — | — | — |
| | 2.3 | 51.01 | 5.58 | 0.53 | — | — | — |
| | 6.2 | 53.48 | 5.09 | 0.45 | — | — | — |
| | 10.9 | 56.11 | 5.44 | 0.34 | — | — | — |
| Borax: Boric Acid 7 : 3 | 0 | 48.43 | 6.67 | 0.47 | 13.6 | 45.5 | 36. |
| | 1.5 | 45.50 | 6.51 | 0.51 | 21.2 | 42.1 | 33. |
| | 3.2 | 47.88 | 6.29 | 0.55 | 14.2 | 41.0 | 44. |
| | 6.1 | 49.85 | 5.98 | 0.50 | 17.8 | 37.8 | 25. |
| | 14.3 | 50.14 | 6.93 | — | — | — | — |

simulated by application of the tar in methanol to asbestos fabric, drying and then determining burning rates of strips of the material inclined at 45° to the horizontal. Results of this nature are given in Table 9, where it

Table 9. The Inflammability Characteristics of Tars Isolated During the Controlled Combustion of Various Celluloses

| Source of Tar | Add-On of Tar mgs/cm² of Asbestos | Burning Rate cms/sec. |
|---|---|---|
| Absorbent Cotton | 32.4 | 0.081 |
| | 29.8 | 0.088 |
| | 27.4 | 0.096 |
| | 25.5 | 0.106 |
| Absorbent Cotton + | 26 1 | 0.082 |
| 9% Borax:Boric Acid | 25.6 | 0.082 |
| (7:3) | 22.4 | 0.081 |
| | 22.1 | 0.101 |
| Absorbent Cotton + | 32.1 | 0.110 |
| 10% Boric Acid | 22.3 | 0.106 |
| | 21.6 | 0.103 |
| | 19.1 | 0 125 |
| Absorbent Cotton + | 25.2 | 0 075 |
| 10% Diammonium | 21.6 | 0 076 |
| Phosphate | 20.9 | 0.083 |

appears that the flame rates vary somewhat in the range of 0.08 to 0.12 centimeters per second irrespective of their concentration from 20 to 30 milligrams per square centimeter of fabric, and although the propagation is somewhat lower for the effective borate and phosphate products, the difference is not sufficient to be a major factor in flameproofing effects. It is to be noted here that the tar concentrations are somewhat in excess of those normally generated at a burning fabric surface where it is usually about 10 to 15 milligrams per square centimeter of fabric.

The tarry products are only slightly volatile except at elevated temperatures, where they change their characteristics rapidly either by cracking or polymerization processes. They exhibit high solubility in methanol, lesser solubility in water, higher alcohols and ketones and low solubility in hydrocarbon solvents On the basis of their fractional solubility in solvents of various polarities they may be separated into less homogeneous mixtures, but these fractions are similar in chemical behavior Retardants appear to influence burning by limiting the quantity rather than significantly affecting the quality factors of this phase.

### 3. Solid Phase Products

The solid decomposition products resulting from the pyrolysis or controlled combustion of fireproofed fabrics consist of a carbonaceous residue

derived from the cellulose itself as well as the thermal remnants from t
added retardant. The rate of fabric decomposition and the resultant cl
production may be followed in an approximate manner by a study of t
total residue obtained at various time intervals via use of the equipme
previously described in Figure 15. During the early stages of the controll

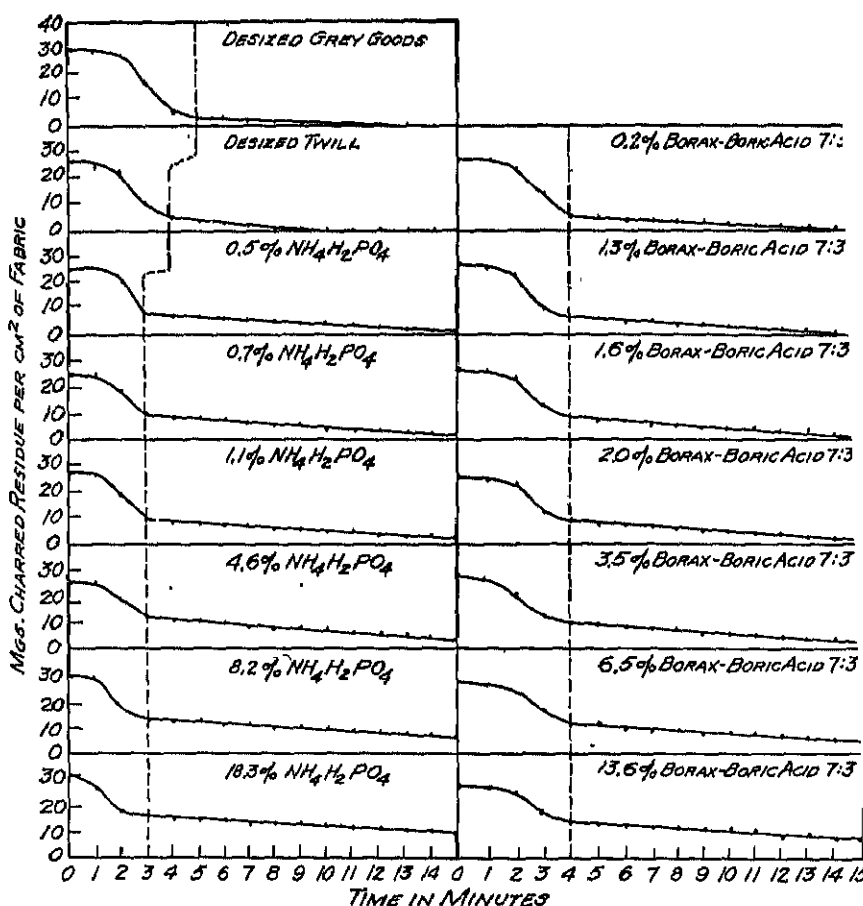



Figure 22. The effect of the phosphate and borate types of retardants on the rate of fabric disintegration during controlled combustion. (The per cent values are those added to desized twill.)

combustion, the fabric enters a short period of temperature elevation accompanied by only slight weight losses as shown in Figure 22. The duration of this induction period depends to a great extent upon the type of retardant as has been pointed out in an earlier section. However, once the fabric has reached a temperature above 300° C., rapid deterioration proceeds with the evolution of tarry materials and a consequent rapid drop

in the yield of solid products. As seen in Figure 22, the second stage is again dependent upon the type of the retardant, the phosphate completing the rapid disintegration in less time than the borate type. On completion of the tar evolution a true char exists, whose further decomposition proceeds slowly via the oxidation of its carbon content to leave finally an ash of the added retardant. The over-all velocity of the latter oxidation reaction is quite uniform and independent of the amount or type of retardant as indicated by the similarity of slope in the linear sections of the curves of Figure 22.

This equality of char oxidation velocities is surprising since the two retardant types exhibit entirely different behavior in practical burning tests. The borate-treated fabrics show very pronounced tendencies to continue glowing after flame propagation has ceased, while the phosphate-treated ones suffer no flameless combustion. It would appear then that at least under these conditions the glowing of chars is not related directly to their over-all oxidation rates. However, the nature of this oxidation and the aspect of the charred residues is entirely different. The non-glowing materials shrink in dimensions with total retention of the original fabric structure, oxidation proceeding uniformly throughout the mass of the char. On the other hand, the glowing type of material as exemplified by the borate-treated fabric is oxidized very non-uniformly with partial to complete ashing of various locations in the char and non-retention of the original woven structure The latter chars are coarse and brittle carbon masses which powder very readily while those from phosphate-treated fabrics are fine textured and relatively strong carbonized fibrous materials. The entirely different aspects of the chars from the various types of retardants are pictured in Figure 23. (*See facing page* 55.)

The various resistances to the glowing phenomenon are the most important property of the solid phase decomposition products of cellulose, and for a complete study a direct isolation of this reaction is required. The separation of the flaming from the glowing reaction is easily accomplished by first carrying out the disintegration in the absence of air. The system in Figure 24 is convenient, where either nitrogen or carbon dioxide enters a preheating section of the furnace at a required rate and passes over the fabric in the decomposition section. The fabric is maintained on the junction of a thermocouple which is inserted in a replaceable inner tube, the lower section of which collects the tarry products After completion of the disintegration the fabric residue is raised to the upper section of the equipment, where it is cooled in an atmosphere of cold $CO_2$ from "dry-ice."

The fabric used in these experiments is an 8 × 5 cm. specimen rolled in the form of a cylinder. After the disintegration in the absence of air, its oxidizing properties may be studied by replacing the $CO_2$ with an air atmosphere or the char may be removed entirely from the furnace and

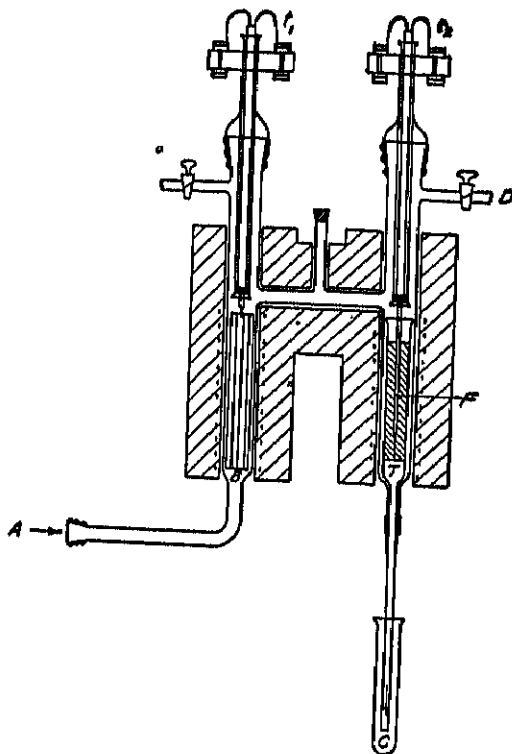



Figure 24. Equipment
thermal decomposition
rics in controlled atmos

*A:* gas inlet; *B:* pre
section at temperature
combustion tube; *F:* fa
temperature $t_2$; *C:* gas e
cooling gas inlet.

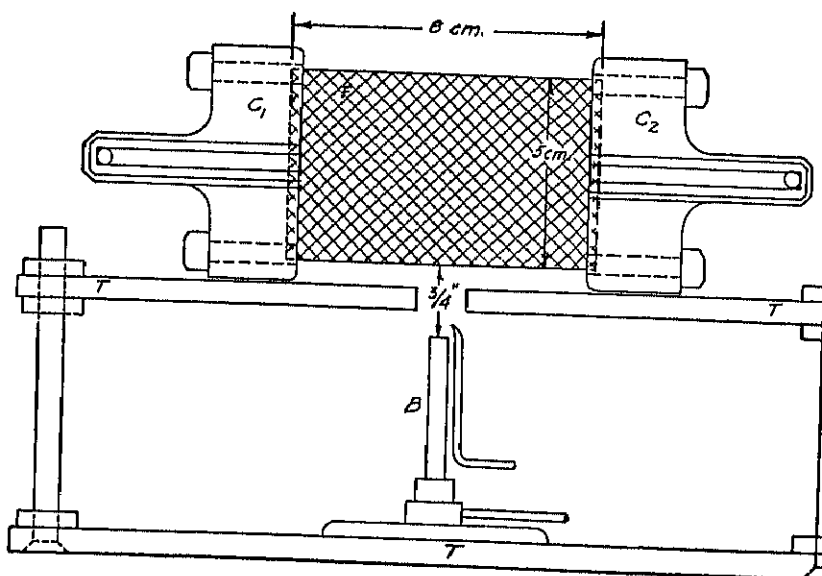



Figure 25. Equipment for determining the glowing characteristics of the cha
residues from the thermal decomposition of treated fabrics. *B:* microburner with p
light; $C_1$, $C_2$: paper clamps; *F:* charred fabric; *T:* transit stand.

subjected to a practical isolated glow test similar to that used in the regular Vertical flame testing procedures. The unrolled char is suspended between paper clamps over a microburner as shown in Figure 25. The flame is 1¾ inches in height and is just non-luminous. Its duration is 12 seconds, and the persistence of the flameless combustion is timed from the removal of the flame source until cessation of glowing. The extent of oxidation in this test is measured by the weight loss suffered due to contact with the flame source and the subsequent oxidation by the glowing reaction.

Table 10. Effect of Small Amounts of Retardants on the Extent and Duration of the Isolated Glowing Reaction of the Chars from Cotton Fabrics

| Retardant | Add-On % | No. of Leachings | Initial Fabric Wt. | Loss During Pyrolysis mgs/cm² of fabric | Loss Via Glow | Glowing Time sec. |
|---|---|---|---|---|---|---|
| Ammonium | 0 | 0 | 26.90 | 21.40 | 5.08 | 73 |
| Dihydrogen | 0.05 | 0 | 24.36 | 18.40 | 2.40 | 78 |
| Phosphate | 0.1 | 0 | 24.50 | 19.58 | 2.74 | 70 |
| | 0.25 | 0 | 24.82 | 18.30 | 3.45 | 94 |
| | 0.5 | 0 | 24.66 | 16.99 | 0.77 | 9 |
| | 1.0 | 0 | 24.05 | 15.71 | 0.33 | 0 |
| | 15.0 | 0 | 33.30 | 17.20 | 0.07 | 0 |
| | 15.0 | 1 | 27 62 | 17.81 | 0.44 | 0 |
| | 15.0 | 2 | 26.31 | 20.05 | 0.65 | 27 |
| | 15.0 | 3 | 28.73 | 20.21 | 0 82 | 45 |
| | 15.0 | 4 | 28.10 | 23 26 | 4.14 | 210 |
| | 15.0 | 5 | 28 27 | 23 67 | 3.64 | 195 |
| Commercial | 0 | 0 | 26.90 | 21 40 | 5.08 | 73 |
| Sulfamate: | 0.05 | 0 | 25 77 | 20 94 | 3 47 | 90 |
| Phosphate | 0.1 | 0 | 25 98 | 20 61 | 4 02 | 120 |
| Mixture | 0.5 | 0 | 22 77 | 16.57 | 3 04 | 78 |
| | 1.0 | 0 | 24.87 | 16 94 | 0.78 | 20 |
| | 15 0 | 0 | 32 11 | 17.51 | 0.03 | 0 |
| | 15.0 | 1 | 28 67 | 19.14 | 1 12 | 0 |
| | 15.0 | 2 | 28 88 | 23.39 | 2.29 | 145 |
| | 15.0 | 3 | 27.38 | 22.54 | 3.81 | 240 |
| | 15 0 | 4 | 28 61 | 23 45 | 4.59 | 215 |
| | 15.0 | 5 | 28.07 | 22.75 | 4 09 | 185 |

Preparation of chars from various fabrics at a nitrogen velocity of 400 cc. per minute and a temperature of 350° C. leads to the results of Table 10, wherein the effects of the phosphate and sulfamate mixture types of retardant are shown in comparison with the untreated fabric. It appears that very decided resistance to glow is imparted to cotton by the addition of small amounts of these materials, the phosphate being the most efficient. In the case of the phosphate, complete resistance to flameless combustion is obtained upon the addition of from 0.5 to 1.0% to the fabric, while continued addition seems to affect only the amount of oxidation ensuing in the presence of the flame source as indicated by the lower loss during

the glow test. The ease with which the inhibiting materials are on static leaching for 15 minutes in water is also demonstrated, tardants being reduced presumably below the minimum requir more than one mild water leaching process.

Similar experiments on a number of retardants and retardant are reported in Table 11. Here it appears that an inert and ir

Table 11. Effect of Large Amounts of Retardants on the Extent and Dura Isolated Glowing Reaction of the Chars from Cotton Fabrics

| Retardant | Add-On % | Initial Fabric Wt. | Loss During Pyrolysis | Loss Vi Glow |
|---|---|---|---|---|
| | | mgs/cm² of fabric | | |
| None | 0 | 26.90 | 21.40 | 5.08 |
| Sodium | 10 | 27.36 | 18.34 | 2.35 |
| Chloride | 20 | 30.66 | 18.51 | 2 64 |
| Ammonium | 10 | 27.92 | 15.07 | 10.55 |
| Sulfamate | 20 | 29.52 | 16 70 | 9.80 |
| | 10 | 27.42 | 16.47 | 7.51 |
| Borax | 30 | 30.71 | 16 96 | 7.66 |
| | 40 | 34.12 | 17.00 | 9 39 |
| Boric Acid | 10 | 24.76 | 13.50 | 0.39 |
| | 20 | 25.48 | 13.80 | 0.35 |
| Ammonium Dihydrogen Phosphate | 10 | 27.64 | 15 26 | 0.07 |
| Borax: Boric Acid (3:7) | 10 | 28.37 | 14 07 | 0.32 |
| Borax: Boric Acid (1:1) | 10 | 26.30 | 13 20 | 1 22 |
| | 20 | 28.52 | 13 26 | 0.28 |
| | 5 | 25.42 | 13.58 | 7 86 |
| Borax: Boric Acid (7:3) | 10 | 26.08 | 13.64 | 5 67 |
| | 20 | 29 22 | 15 21 | 0.48 |
| Borax: Boric Acid: Ammonium Dihydrogen Phosphate (1:1:2) | 10 | 30.56 | 15 96 | 0.21 |
| | 20 | 30.73 | 13.15 | 0.20 |
| Borax: Boric Acid: Ammonium Dihydrogen Phosphate (7:3:5) | 10 | 29.75 | 15.18 | 0.21 |
| | 20 | 33.42 | 15.32 | 0.22 |

material such as sodium chloride has little if any effect on the glowing reaction, while the sulfamate and borax appear to accent This is due, probably, to the larger amounts of char remaining a disintegration reaction. However, with the phosphate and boric aci the extent and duration of this reaction are reduced to very low the former being the most efficient in respect to oxidation in the p of the flame source. With mixtures of borax and boric acid, the g tarding component loses its inhibiting effect if the borax compone excess. In the three-component system, which includes the very

phosphate, glow propagation is also reduced to nil although even here the borax appears to exhibit a deleterious action in that the oxidation in the presence of the flame is considerably greater than that obtained with phosphate alone on the char.

These effects indicate the composite nature of the secondary oxidation of the charred residues from fabrics and point to changes in the course rather than to the over-all rate or extent of the reaction as being the important effect brought about by retardants. Preliminary experimentation establishes that the afterglow phenomenon is a general one for carbon

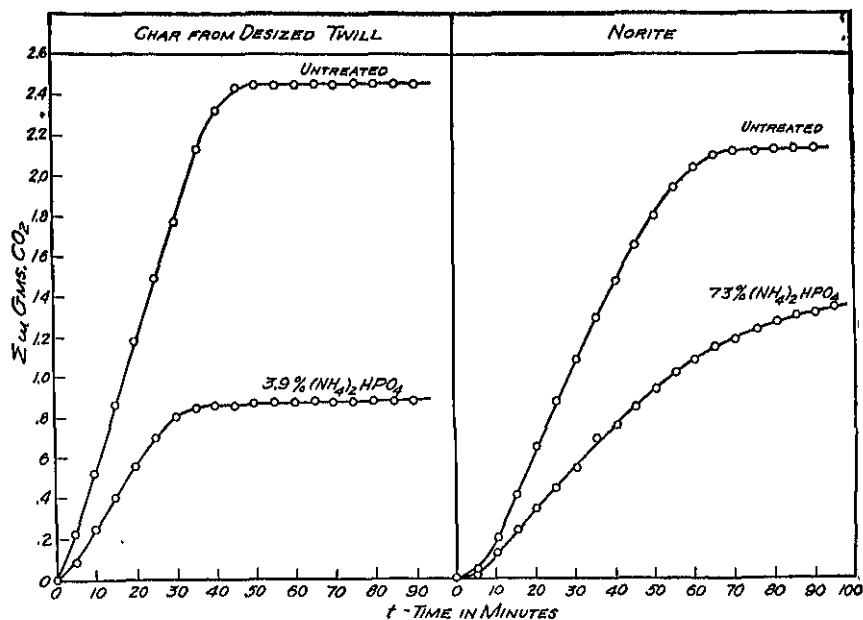



Figure 26. The similarity in the oxidation characteristics of charred residues from fabrics and absorbent carbon as influenced by glow-retarding phosphates

and not confined to fabric residues. This is shown quite readily in Figure 26, where the rate of $CO_2$ evolution is determined both for fabric residues and for Norite absorbent carbon. In each case both the rate and extent of this oxidation is reduced for the addition of ammonium phosphate when oxidation is carried out under identical conditions in a standard "Combustion Train." The standardized combustion conditions of one gram of char at 500° C. and 200 cc. of air per minute arise from an examination of the factors affecting the oxidation reaction for untreated absorbent carbon Here it is found that with variation of the temperatures above 300° C. both the rate and the extent of the oxidation to $CO_2$ increase with increased temperature, but above 600° C. the rate is insensitive to the temperature, while the extent of the reaction continues to increase until

at somewhat above 700° C. the theoretical production of $CO_2$ is a
proached. Similarly, variations of air supply influence the reaction, grea
velocities promoting a more rapid reaction. In the vicinity of 200 cc. of
per minute, increased air supply does not influence either the rate or c
tent of $CO_2$ evolution, which are here solely dependent upon the tempe
ture and amount of carbon present. Further examination shows that wi
variation of the carbon concentration from 0.25 to 1.0 gms., little if a
change in the $CO_2$ rate occurs, while the total amount generated is direct
proportional to the original carbon charge. The chosen conditions
500° C. and 200 cc. of air per minute per gram of carbon are hence co
sidered ideal for comparative studies of this kind.

For thorough studies on the kinetics of the oxidation of charred fabr
residues, the equipment of Figure 27 provides a rapid and convenie

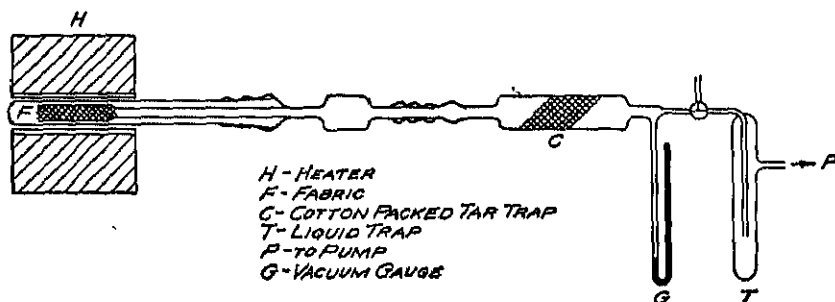



Figure 27. Pyrolytic equipment for the production of charred residues from fabrics for further oxidative studies.

means for producing chars from variously treated materials. Here the
fabric is decomposed under pyrolysis conditions of 500° C. and less than
5 mm. Hg. absolute pressure for various periods of time. On cooling, the
residual char is removed and one gram is inserted on the thermocouple
junction of the equipment shown in Figure 28. Dry and $CO_2$-free air at
200 cc. per minute passes over the char where the initiating temperature
is 500° C. The carbon dioxide evolution is determined at various time intervals at the absorbent system $C_1$ and $C_2$ while the residual CO is further oxidized by passage over hot copper oxide and is determined at time intervals by absorption at $C_4$ and $C_5$.

In the oxidation of the char, the course and rate of the various reactions appear to be dependent not only on the retardant but also upon the completeness of the pyrolysis. Higher temperatures and pyrolysis times provide for more complete tar generation and give better differentiation for the course of the oxidation of chars from treated and untreated fabrics. These effects are shown in Figure 29, where a fabric containing 5% of diammonium phosphate is compared with the original untreated cotton.

The phosphate apparently changes the course of the oxidation, favoring the production of CO rather than $CO_2$, and the effect is most apparent for

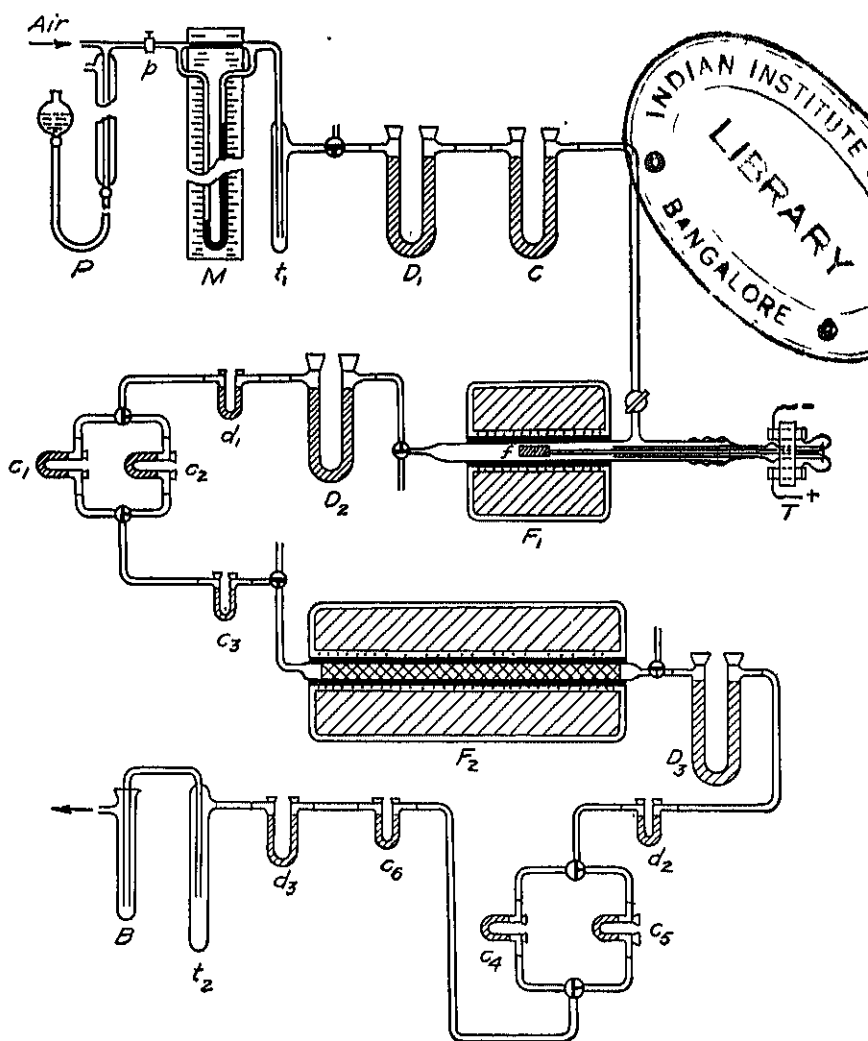



Figure 28. Equipment for kinetic studies on the oxidation of charred residues from fabrics

$P$, $M$, $t_1$: air inlet system; $D_1$, $C$: purification of inlet air; $F_1$, $f$, $T$: oxidative system for char; $D_2$, $D_1$, $C_1$, $C_2$, $C_3$: $CO_2$ determination system; $F_2$: CO oxidation system; $D_3$, $d_2$, $C_4$, $C_5$, $C_6$: CO determination system; $d_3$, $t_2$, $B$: gas exit system

chars prepared by lengthy pyrolysis. Similar effects are shown for pyrolysis at 550° C. in Figure 30, where the promotion of CO formation is even more apparent with increased completeness of pyrolysis.

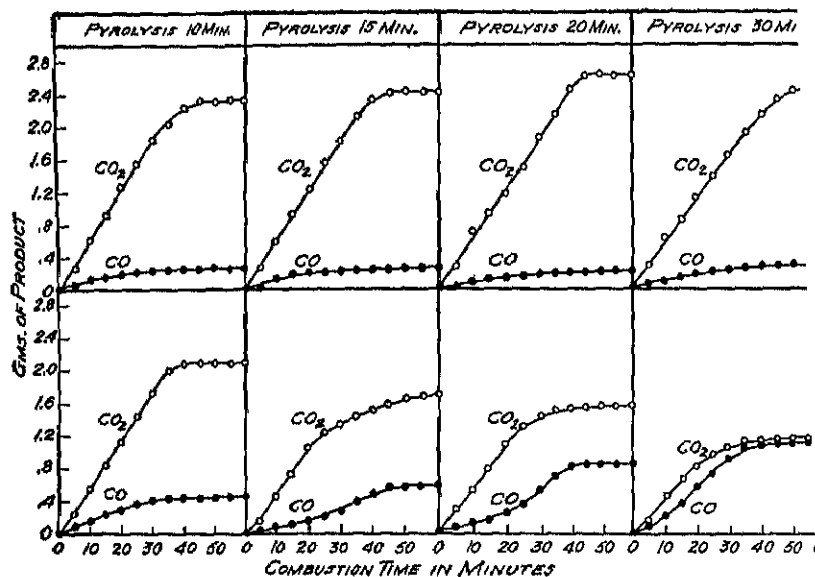



Figure 29. Comparative data for untreated fabric and that treated with 5% di
monium phosphate, showing the influence of the retardant in altering the course
the oxidation of the charred residues from these fabrics.

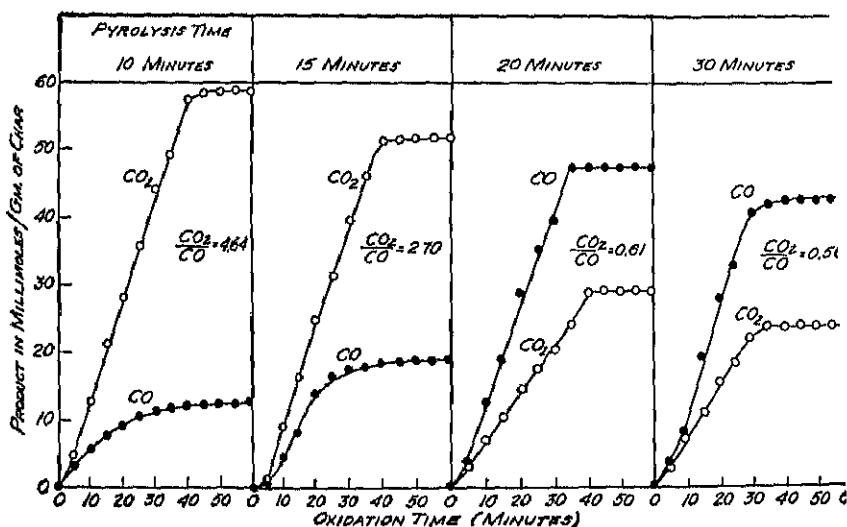



Figure 30. The influence of 4% diammonium phosphate in promoting the oxida
tion of charred residues from fabrics in the direction of CO rather than $CO_2$; a func
tion of the completeness of the preliminary pyrolysis to eliminate the tarry product
responsible for flaming.

The agreement between the course of char oxidation and the tendency for flameless combustion is demonstrated in Figure 31. Here the very efficient phosphate glow retardant reduces the $CO_2$ evolution from 2.5 to 0.8 grams per gram of char for additions as low as 1% of the retardant to the fabric, and this reduction is not affected appreciably by further additions of the phosphate. Similar effects are obtained for the fairly effective boric acid where again the $CO_2$ evolution is reduced, but not to the extent of that obtained for the phosphate, the minimum value being about 1.2 grams of $CO_2$ per gram of char irrespective of the amount of boric acid added originally to the fabric. However, with a glowing type of retardant such as borax, small additions have little if any effect on the course of the oxidation of the resultant char, and even for higher amounts the value never falls below 2.0 grams of $CO_2$ per gram of char. These results are in direct accord with the observed facts that quantities of ammonium phosphate or boric acid as low as 1% will prevent glow propagation but that borax although inhibiting flame propagation will not prevent the travel of flameless combustion in a fabric, irrespective of the amount of the retardant. The prime difference apparently lies in the relative abilities of these retardants to promote the oxidation of charred fabric residues to the monoxide rather than the dioxide state of carbon.

Charred residues obtained from the pyrolysis of glowproofed fabrics retain their non-glowing characteristics even after 14 hours' extraction with hot water in a modified Soxhlet apparatus Further extraction for 5 hours with methanol, refluxing for 1 hour with 0.1 N. NaOH and 14 hours' additional water extraction have no further effect on an originally glowproofed char. This resistance is exhibited by the phosphate- and boric acid-treated materials and their blends with borax Apparently the borax component is removed quite readily by the extraction, leaving the glowproofing agent alone on the char.

Chars from untreated cotton fabric and those from material treated with borax glow very readily, but when these chars are impregnated with either boric acid or diammonium phosphate the glowing tendency is greatly reduced These investigations indicate that the physical form or state of the carbon is not a governing factor, since chars of the glowing type may be converted to the non-glowing type by simple addition of the anti-glow agent

The tenacity with which $(NH_4)_2HPO_4$ is retained after pyrolysis is dependent to some extent upon the presence of other materials in the charred residue. Mixtures of glow retardants with borax are not retained nearly so well as is the anti-glow reagent alone, while borax alone is removed very quickly by extraction. The analyses of the charred residues both before and after extraction show that practically all the originally added phosphate is retained by the char as demonstrated by Table 12, and its retention appears to be independent of the extent of the pyrolysis. However,

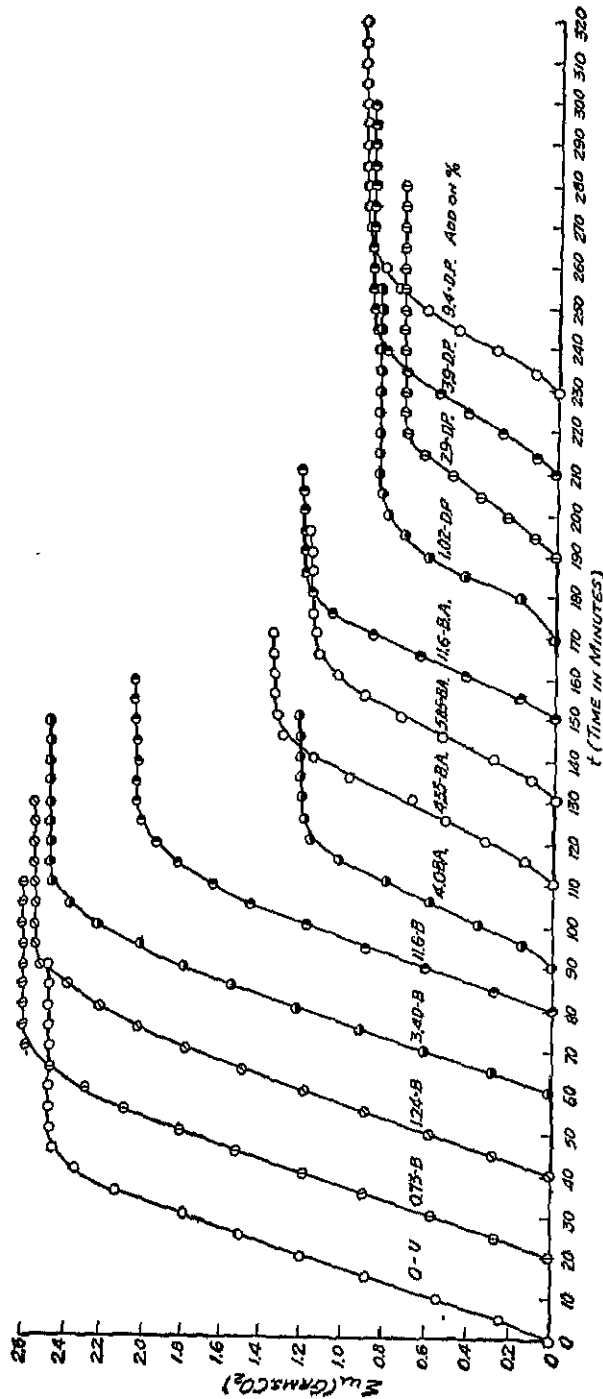



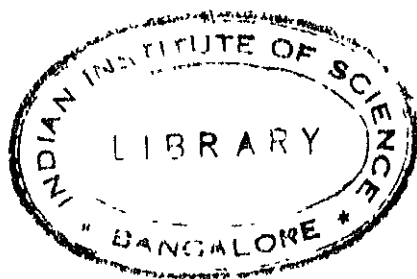
Figure 31. The effect of various retardants on the evolution of carbon dioxide during the oxidation of the charred residues from cotton fabrics.

Chars from—*U*: untreated fabric; *B*: borax treated; *B.A.*: boric acid treated; and *D.P.*: diammonium phosphate treated fabric. The per cent values are those added originally to the desized twill.

Table 12. Composition of the Pyrolytic Chars from Various Fabrics

| | Theory ($C_6H_{10}O_5$) | Untreated | 5% $(NH_4)_2HPO_4$ Before Extraction | After Extraction | 5% Borax Before Extraction | After Extraction |
|---|---|---|---|---|---|---|
| C % | 44.4 | 85.28 | 78.65 | 79.14 | 77.38 | 87.33 |
| H % | 6.2 | 3.40 | 3.04 | 3.49 | 3.19 | 3.98 |
| Ash % | 0 | 3.60 | 2.99 | 3.57 | 9.29 | 0.76 |
| $H_3PO_4$ % | 0 | 0 | 6.95 | 7.7 | 0 | 0 |
| $H_2O$ Soluble | 0 | 0.1 | – 1.4 | 0 | 15.9 | 0 |

mixture of the phosphate with borax lowers the $H_3PO_4$ retention somewhat, probably due to the $Na_3PO_4$ formation.

X-ray diffraction patterns of the fabrics, both before and after pyrolysis and extraction, indicate that at most the retention of the glow retardant is due to a surface intermicellar reaction. The patterns for the treated fabrics are identical with those from cellulose and the patterns obtained from the pyrolyzed and extracted chars are consistent with those from carbon.

# Chapter III

## Mechanisms of Flameproofing

*S. Coppick*

Although the literature on the subject of flameproofing is quite
the majority of the experiments performed have been of a practi
dealing with the development of new and improved flame-reta
terials and methods of application. For this reason, there is litt
mental data available pertaining to the fundamentals of flan
agents and the mechanisms by which they function. In the a
supporting data, there has been in the past considerable specula
these mechanisms and, as a result, several different explanatio
phenomenon of flame retardation have been proposed. In con
phenomenon of afterglow has only in recent years been recogni
independent corollary of afterflaming and hence has not been t
of such extensive speculation. In further advances into the field
proofing, it is highly desirable that future experiments be based,
theoretical speculations, but rather upon fundamental mechanis
have some foundation in fact.

In the preceding chapter, flame-retarding materials were show
a specific influence upon the rate and extent of formation of th
degradation products of cellulose. This influence may be regard
primary effect of flameproofing action. It would be well, therefore
further into the fundamental mechanisms in an attempt to un
basic causes of these primary effects. Consequently, the followin
has been devoted to consideration of the mechanisms of the prev
afterflame and afterglow. An attempt has been made to discuss
the mechanisms advanced, placing proper emphasis upon those
pear to have a better foundation in experimental fact. It is quite
that considerable additional experimentation is called for on th
fundamental aspects of flameproofing.

### A. PREVENTION OF AFTERFLAMING

#### 1. Chemical Theories

An examination of the composition of the efficient fire-retardin
cals reveals that with only a few exceptions they include those

which might be expected to enhance the decomposition of cellulose under the influence of heat. Moreover, the majority of retardants have an appreciable degrading action on cellulose even at normal or slightly elevated temperature or when subjected to sunlight. At first this would appear to be contrary to their retarding action in the presence of a flame, but it is to be remembered that flameproofing does not involve protection from damage to that area in the vicinity of the heat source, but simply excludes propagation of the flaming reaction.

The most common agents which have a pronounced degrading action on cellulose are the strong alkalies, the mineral acids and oxidizing agents as shown in Chapter II, and it appears to be more than a coincidence that these should be the materials most effective as fire retardants. It is not necessary that these degrading chemicals be used directly due to their pronounced tendering effects under atmospheric conditions, but a more practical method is to provide such combinations that will produce the active ingredient under the influence of heat from the flame source. On this basis the theory has been proposed that the flame-retarding effects shown by many substances are due to their promoting the breakdown of the cellulose at high temperature in a direction other than that which takes place in their absence.

The substances which produce strong alkali at high temperatures include the alkali salts of weak acids, *i.e.*, borax, sodium carbonate and bicarbonate, sodium tungstate, silicate, stannate, molybdate, aluminate, and arsenate. None of the neutral salts of strong acids and bases are subject to marked decomposition at flame temperatures and to produce strong acids, the salt with a weak base is preferred. Those most easily decomposed are the ammonium salts and include the phosphates, sulfamate, sulfate and halides, although calcium, magnesium and zinc chloride are relatively unstable and have a pronounced flame-retarding effect The easily reducible oxides are well known in their degrading action on cellulose and may be used directly or in the hydroxide or hydrated form which include ferric, stannic, arsenic, chromic and titanic. The standard oxidants and oxidation promoters such as potassium nitrate, the metallic chromates, silenium, potassium permanganate and thiocyanate are also fairly effective retardants [1]

Evidence in favor of this theory is given by Ramsbottom and Snoad [1] who limited their intensive investigations to the borax-boric acid system, and by Metz,[2] Serebrennikov,[3] Palmer,[4] and Richardson [5] in their studies

[1] Ramsbottom, J. E., and Snoad, A. W., Dept. of Scientific and Industrial Research, Great Britain, Second Report of the Fabrics Co-ordinating Research Committee (1930)

[2] Metz, L., *Gasschutz U Luftschutz*, 6, 260 (1936)

[3] Serebrennikov, P. P., U. S. Forest Service Div of Silvics, Translation, 9, 151 (1934).

[4] Palmer, R. W., *Ind. Eng Chem*, 10, 264 (1918).

[5] Richardson, N. A., *J. Soc. Chem. Ind.*, 56, 202 (1937).

on the fireproofing of woody materials. The data indicate that the effectiv chemicals alter the course of cellulosic decomposition favoring the forma tion of lesser amounts of inflammable tars and gases and increasing th production of non-volatile carbonaceous material. The theory is also i direct accord with the effects shown in the pyrolysis and controlled com bustion studies of Chapter II, wherein marked decreases in both th amount and concentration of the available tarry fuel supply are observe on the addition of the retarding chemical, and this fraction is directly related to the flaming characteristics of the fabric.

A schematic summary of the change in the course of cellulosic fission brought about by retardants is given in Figure 1. Here the normal reaction

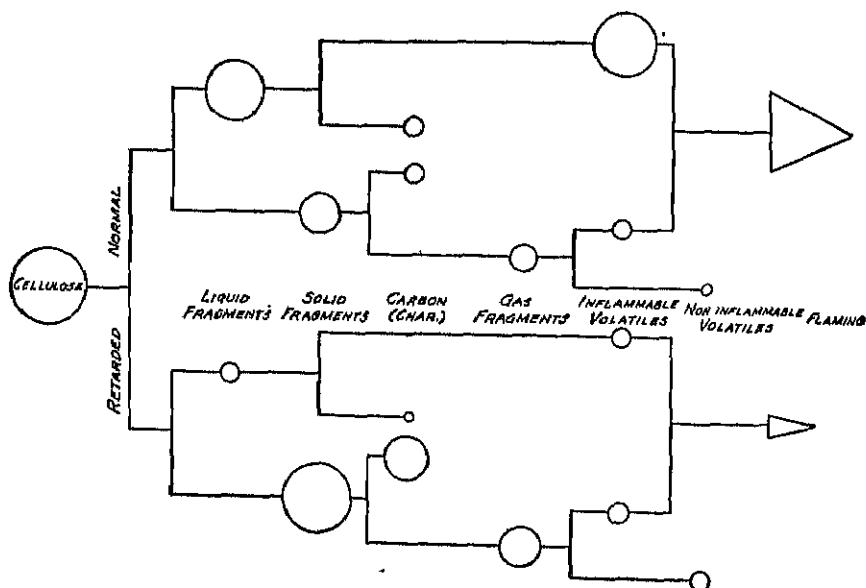
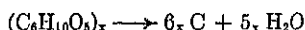



Figure 1. Schematic representations for the path of the thermal degradation of cellulose in the presence and absence of retardants, and the relation to the flaming characteristics. The size of the spheres represents approximate quantities of the various fission products.

is pictured as proceeding initially to give large quantities of volatile and relatively low molecular weight fragments which are easily cracked and oxidized in the vapor phase and constitute the flaming interface. The small amount of non-volatile charred residue is further decomposed to give minor amounts of gas and carbon, the latter being susceptible to oxidation by the flameless combustion reaction. In the presence of the directing influence of retardants, however, the course of the reaction appears to be toward fission of fragments of much greater molecular magnitude or of such structure to promote lesser volatility. The small amount of low

molecular weight tars pass off as before but their quantity is insufficient to support a continuance of the flaming interface. The non-volatile constituents are cracked in a solid phase reaction giving rise to larger amounts of gases and carbon than in the normal reaction. It appears that the critical reaction is the highly exothermic oxidative cracking of the degradation fragments, and it is essential that this process be confined to the solid phase if flaming is to be eliminated. The function of the retardant will then be to promote the initial breakdown in the direction of non-volatile fragments either by changing their relative size, molecular complexity or the nature of their side groupings. Any process such as cyclization, polymerization, polycondensation, or cross-bridging of these fragments should be effective in promoting their retention of the solid phase at high temperatures.

One of the specific mechanisms for the preferred course of cellulosic decomposition in the presence of a retardant would be the ideal where the whole of the carbon content would be confined to the solid phase. This involves a catalytic dehydration process such that the following prevails:

$$(C_6H_{10}O_5)_x \longrightarrow 6_x\,C + 5_x\,H_2O$$

All fragments are thus confined to non-volatile carbon, and flaming cannot ensue. This mechanism has been proposed by Leatherman[6] to explain the retardant action of metallic oxides, particularly the hydrated stannic oxide as originally used in the Perkin[7] process. Similar catalytic pyrogenic decomposition functions are forwarded to explain the action of ferric, manganese, cobalt, antimony, lead, arsenic and zinc oxides, and are compatible with their known dehydrative activity in other reactions The theory has been extended to cover a large number of the soluble inorganic salts which decompose at flame temperatures to produce desiccant materials such as $NaOH$, $H_2SO_4$, $H_3PO_4$, $NH_2HSO_3$, etc., and is substantiated by Leatherman's[6] studies where heating of untreated fabrics and those treated with metallic oxides is conducted in a stream of air. Considerably more carbon is set free in the case of the treated fabrics, and in similar rapid heating experiments the water liberated from treated fabric is equivalent to about twice that normally produced from the untreated material. These results are in agreement with those of the combustion and pyrolysis studies described in Chapter II; however, the variation of the amount of water liberated with the quantity of added retardant is not quite sufficient to be accepted as conclusive evidence for the wide adaptability of the mechanism.

Another fundamental mechanism of wider applicability is that stimu-

[6] Leatherman, M., U. S. Dept. of Agriculture, Circ. No. 466 (March, 1938).

[7] Perkin, W. H., 8th Internat'l. Cong. Appl. Chem., Washington and New York, 28: 119–134 (1912).

lated by the observation of Sisson[8] that the majority of the flame-retarding chemicals contain groupings which are active in hy bridging processes. The well-ordered and relatively inactive po cellulose is considered to involve the hydrogen bonding between hydroxyls, while the disordered and active portions are characte the bridging of adjacent chains via water molecules.[9, 10, 11] The st stability of the system is critically related to these intermolecula and it is proposed that upon contact with high temperature sou bridging media are lost due to the thermal activity of water temperatures, but that the linkage may be maintained if a non- component of sufficient hydrogen-bonding activity is present. T tronic configurations which promote strong linkages of this typ cellulose system are =O, —OH and —$NH_2$. These groupings are larly prevalent in the more efficient retardants such as the pho sulfates and sulfamates, and the theory proposes that thermal s and the confining of fragments to the solid phase is due to a grea to the hydrogen-bonding capacity of these compounds. It is pointed out that the main chemical characteristic of the strong d tors and the hydrated salts effective in retardant action is thei hydrogen-bonding power, and although they prefer to stabilize th tronic configuration by bonding with water, in the absence of the la cellulosic hydroxyl serves the same function.

It has been observed in many instances that the thermal stabilit cellulose chain as a whole is intimately associated with the activit alcoholic groups. Thus, fission of the glucosidic linkages by the hy or oxidative process takes place much less readily if the hydrox inactivated by substitution as exemplified by the relative stability cellulose derivatives. The acidic retardants may then function not their capacity for side group inactivation by hydrogen bonding but direct substitution at flame temperatures. The bi- and tri-function the phosphates, sulfates, and sulfamates also provides for cross- through primary bonds to create further difficulties in the splittin volatile chain fragments. This three-dimensional effect may proce via polymerization or condensation of aldehydic groupings as ca by the strong acid or alkali thermal dissociation product of the ret

## 2. Coating Theories

As early as 1820, attention was called to the fact that among th known flame-retarding salts there exists a group which have a low 

[8] Sisson, W. A., Amer. Viscose Corp., discussions with the writer.
[9] Huggins, M., *J. Org. Chem.*, 1, 407 (1936).
[10] Heuser, E., "The Chemistry of Cellulose," John Wiley and Sons, No (1944).
[11] Mark, H., *Chem. Revs.*, 26, 169, 181 (1940).

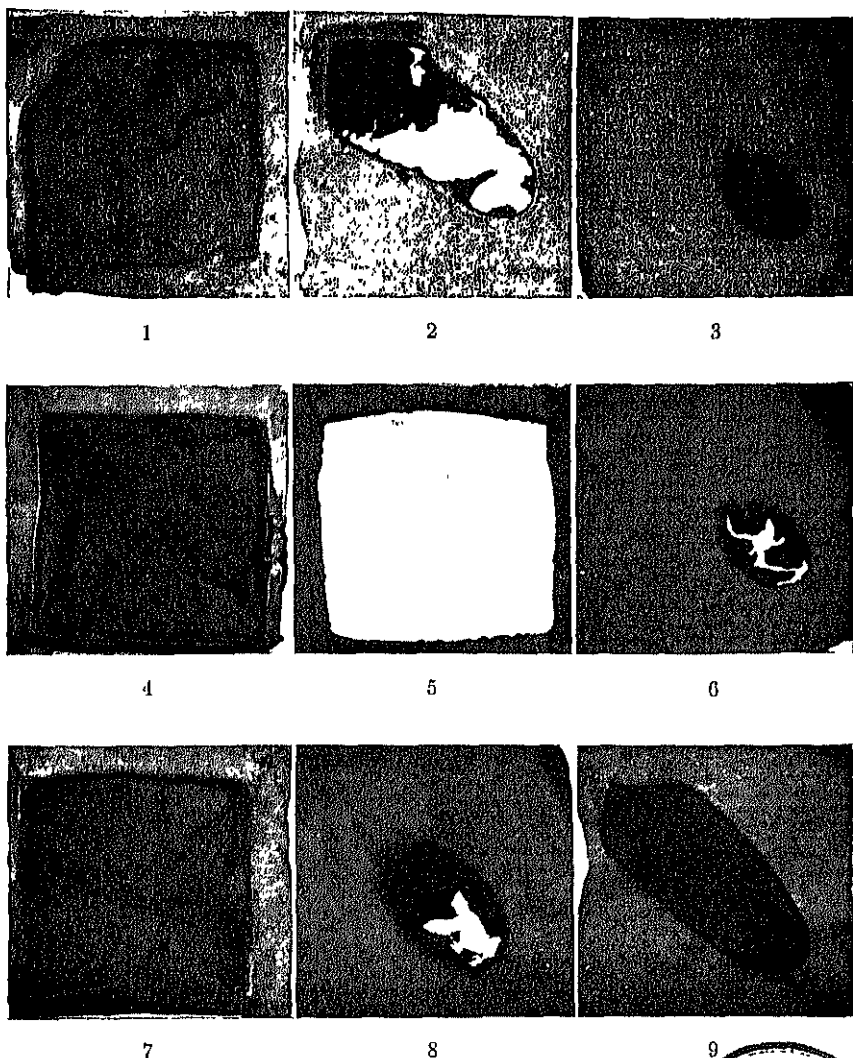
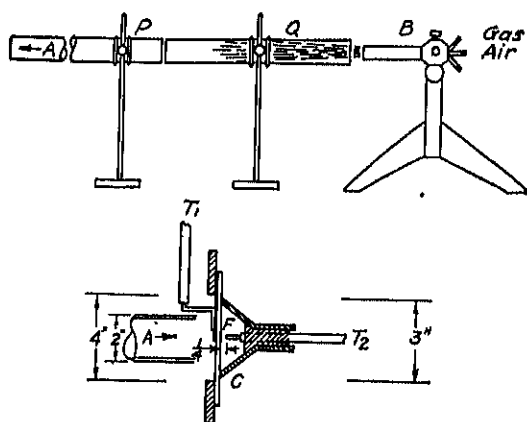



Figure 2. 45°-Microburner flame test specimens.

1. 9% Boric acid ($H_3BO_3$)
2. 16% Borax ($Na_2B_4O_7 \cdot 10H_2O$)
3. 13% Borax:Boric acid (1:1)
4. 9% Boric acid ($H_3BO_3$)
5. 9% Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)
6. 10% Trisodium phosphate:Boric acid (1:1)
7. 9% Boric acid ($H_3BO_3$)
8. 9% Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$)
9. 12% Aluminum sulfate:Boric acid (1:1)

$B$: burner; $Q$: quartz tube, $P$: pyrex tube; $F$: fabric; $C$: funnel; $A$: flame direction; $T_1$, $T_2$: thermocouples.

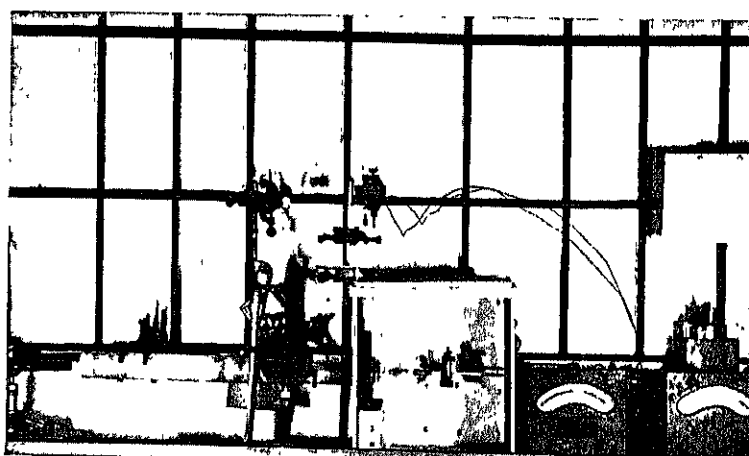



Figure 6. Equipment for studies of the insulation value of glowproofed fab

point and upon contact with a flame fuse to cover the fabric with a glassy layer. Upon this Gay-Lussac[12] advanced the postulation that one of the mechanisms for flameproofing action involves the coating of cellulose with a non-penetrable skin whereby oxygen exclusion functions to prevent propagation of the combustion reaction. Various modifications of the original hypothesis have been forwarded, and the theory is very prevalent in recent literature.

The action of the borates has been explained on this basis and the theory is particularly suitable for considerations regarding the specific and anomalous behavior of the efficient mixtures of borax and boric acid. In researches conducted by the British Air Ministry,[1] this flameproofing system was investigated with considerable thoroughness, and it is pointed out that although each of the components alone performs a coating function, the mixture acts much more efficiently. Both borax and boric acid leave a badly distributed and poorly adhering crystalline deposit on a fabric, while the mixture has very little crystallizing tendency and on evaporation of the water leaves a glassy matrix which forms a tightly adhering and almost invisible covering over the cotton fibers Charring tests indicate that this two-component layer is more impervious to air than are its constituents alone.

Heretofore, attention has been directed to the desirability for the formation of a vitreous layer or skin on the fiber surface; however, it appears that the most effective coating is one of less glassy nature Investigations with mixtures of various salts show that there are wide variations in the respective abilities of certain blends to form frothy products when subjected to heat sources of an intensity comparable to flame temperatures Moreover, the effectiveness of these mixtures of inorganic compounds in preventing afterflaming is somewhat proportional to their tendencies to form stable foams The superiority of specific mixtures over the simple components is demonstrated in the 45° flame test specimens of Figure 2 The function of the foam appears to be not only to provide protection of the fabric from the air, but also serves as a barrier to the flame and entraps the volatile tars evolved during combustion.

The simple formation of a foam is not the only requirement for efficient flameproofing, although in general the agreement is rather good. For maximum retardant efficiency it is postulated that a two- or three-component system should have such properties that one component at least must decompose at a relatively low temperature with the evolution of large amounts of gaseous products. The decomposition temperature should be in the vicinity of 80 to 200° C. and the resulting gas phase of course must be non-flammable, *i.e.*, either $H_2O$, $CO_2$, $NH_3$ or $SO_2$, etc. One of the other components must melt at a temperature near that at

[12] Gay-Lussac, *Ann. Chim. Phys.*, 18 (1823).

which gas evolution begins, and the mixture should be compati
ing a uniform flux which solidifies as decomposition progre
foam resulting from these series of phase transitions should be a
like structure stable at temperatures in the vicinity of 500° C

The number of inorganic materials which have the desired
is rather limited, and usually not all of the requirements are m
ever, a pronounced foaming tendency usually leads to effective
action although the relative efficiencies may not always follow t
order due to improper foam structure as shown in Table 1. Here
height is reported as that attained when 5 grams of the retar
heated in a test tube of 1-inch diameter for 5 minutes at 450 t

It should be pointed out that this mechanism is not intended
the processes which lead to the effective action of the strong aci
retardant. Here, undoubtedly, the prime cause for flameproofi
tirely different since foaming tendencies for the ammonium pl
sulfamate and bromide are negligible.

## 3. Gas Theories

The hypothesis presumes that flameproofing may be accomp
the impregnation of fabrics with a material which will decompos
at elevated temperatures with the evolution of inert or difficultl
able gases or vapors. Changes in the atmosphere in the vicinity o
ric are supposed to serve either of two functions: the dilution c
flammable gases produced during normal cellulosic decompositio
blanketing effect to exclude or reduce the prevailing oxidizing at
of the environment. The supposition of a quenching action by
evolution is also prevalent in the general concept for mechanism
type. The effect of such changes in the concentration of gaseous
air is presumed to raise the kindling temperature of the vapor m
such an extent that the rate of combustion is reduced, and in
becomes zero, at which point flame propagation ceases.

Among the gases most commonly considered effective are: C
HCl, $H_2O$, and $SO_2$. The theory is hence supported by the flam
action of sodium carbonate and bicarbonate, the ammonium halid
phates and sulphates, the chlorides of zinc, calcium and magnesiu
hydrated salts such as borax and aluminum sulphate, and by am
sulfamate.

The relative efficiencies of the flame retardants which might fun
this mechanism should depend upon several factors. The availa
gas supply, the decomposition temperature and the rate of gas
in the required temperature range should be the determinants. I
erally conceded that rapid gas evolution should proceed from the r
at temperatures in the vicinity of that at which the cellulo

Table 1. Correlation Between Foaming Tendency and Flame Retardancy

| Relative Efficiency Based Upon the Volume of Foam Formed (Ht. of Foam in 1" diam Tube) | | | Relative Efficiency Based Upon Performance in the 45°-Microburner Flame Test | | | | |
|---|---|---|---|---|---|---|---|
| | Flame Retardant | Foam Ht. in. | | Flame Retardant | Add-On % | Char Area $in.^2$ | After-flame sec. |
| 1 | Boric Acid : Ammonium Dihydrogen Phosphate (1:1) | 4.50 | 1 | Boric Acid : Ammonium Dihydrogen Phosphate (1:1) | 15.0 | 1.44 | 0 |
| 2 | Borax : Boric Acid (1:1) | 3 50 | 2 | Borax : Boric Acid (1:1) | 7.7 | 1.67 | 0 |
| 3 | *Sodium Phosphate : Boric Acid* (1:1) | 3 50 | 4 | Borax : Boric Acid : Diammonium Phosphate (7:3:5) | 9.5 | 1.90 | 0 |
| 4 | Borax : Boric Acid : Diammonium Phosphate (7:3:5) | 3 25 | 3 | Sodium Phosphate : Boric Acid (1:1) | 10.5 | 2.06 | 0 |
| 5 | Borax : Boric Acid (7 3) | 3.25 | 6 | Commercial Borate Mixture | 8.4 | 2.08 | 0 |
| 6 | Commercial Borate Mixture | 2 75 | 5 | Borax : Boric Acid (7:3) | 9.5 | 2.19 | 0 |
| 7 | Borax : Boric Acid · Diammonium Phosphate (1:1 2) | 2 75 | 8 | Borax : Diammonium Phosphate (1:1) | 7.9 | 2.84 | 0 |
| 8 | Borax : Diammonium Phosphate (1:1) | 2.50 | 7 | Borax : Boric Acid · Diammonium Phosphate (1:1:2) | 8.8 | 2.86 | 0 |
| 9 | Borax | 2 75 | 10 | Aluminum Sulfate | 8.8 | 4.59 | 0 |
| 10 | *Aluminum Sulfate* | 2.00 | 9 | Borax | 15.8 | Burned to end | 39 |
| 11 | Boric Acid | .25 | 11 | Boric Acid | 9.3 | Completely burned | 70 |

decomposes, and a rough estimate places this at about 300° C. for m mum efficiency. Hence, the relatively low temperatures required for decomposition of the ammonium salts, bicarbonates and hydrates ar favor of good performance.

It has been pointed out[13] that although HCl would satisfy all requirements in a mechanism of this type, the compounds which show spontaneity for evolution of this gas, in the required temperature ra usually decompose at appreciable rates either thermally or by hydrol under normal atmospheric conditions. Hence, their tendering effect cellulose renders them of little if any practical importance. Furtherm if more stable HCl donors such as the chlorinated resins are used, the evolution does not proceed at a sufficient rate until temperatures gre in excess of 300° C. are reached, and they do not provide adequate fla proofing when used alone. However, in the presence of a dechlorina catalyst the velocity of gas evolution might be increased at the des temperatures. This is cited as a contributing mechanism for the protec afforded by certain chlorinated materials in the presence of zinc oxid basic zinc carbonate.

From a quantity of gas standpoint, the theory becomes almost tenable when the practical and effective additions of retardants are c pared with the amounts of non-flammable gases produced by the composition of cellulose itself. Experimentation[14] shows that none of well-known retardants produce inert gases in quantities of magnit much greater than the fabric alone. Despite this, however, the theory been widely accepted. The results given in Chapter II certainly do substantiate this mechanism as of prime importance in the flameproo of fabrics, although it may contribute somewhat to the over-all re dation.

## 4. Thermal Theories

It has been proposed that flameproofing may be explained on a ther basis whereby fabric temperatures "in situ" are retained below the sociation point. Two major concepts are prevalent, the first of wh presumes that the calorific input of an incident heat source may be sipated by an endothermic change in the retardant itself. Thus the fus sublimation or decomposition of the retardant as well as any further ph transitions of retardant mixtures might absorb considerable energy wh otherwise would contribute to the amount required for activation of

[13] Leatherman, M., Maj., C.W.S., "Flameproofing of Permeable Military Cl ing," Memorandum Report, T.D.M.R. No. 936, Project No. D3 1-1, Edgew Arsenal, Md. (Nov 25, 1944).

[14] Tyner, H. D., "Fire Extinguishing Effectiveness of Chemicals in Water Soluti *Ind. Eng. Chem.*, 33, 60–5 (1941).

fabric. The second hypothesis supposes that the incident heat may be conducted away from the fibers at a rate comparable to that at which the source supplies it, and thus by effects similar to those encountered in the Davy Safety Lamp the fabric in the vicinity of the edge of the flame never reaches its combustion temperature. However, although little or no experimental evidence has been forwarded for this hypothesis, it would appear that since only small amounts of certain materials are required to be effective as retardants they would have to be extremely efficient in their heat-dissipating capacity in order to substantiate the theory Moreover, there exist a number of salts which are ineffective as retardants although their energy changes are similar to those of the efficient salts. These non-retardants have little or no practical flameproofing value when added in moderate amounts to a fabric and even upon the addition of excessive quantities they will not prevent flame propagation and at most only reduce the rate at which the fabric is consumed. Furthermore, the known heat conduction constants for materials of widely divergent retarding power are either quite similar or are not sufficiently different to account for their dissimilar flameproofing qualities.

Further verification of the inadequacy of this theory to explain the facts is found by a detailed study of the phase transitions involved in the thermal behavior of a large number of retardants when heated to temperatures in the vicinity of that attained by burning fabric When these salts are heated at a constant rate and the differential heating curve determined for equal quantities of retardant components and mixtures, the number of inflections and their magnitude may be taken as being directly proportional to the heat-absorbing capacity of the system Phase data, similar to that depicted in Figure 3, for a large number of materials show that no correlation exists between the number, position and magnitude of the energy changes and the relative ability of the materials to prevent flame propagation In fact, some of the better retardants undergo only minor transitions and in the case of the fairly efficient ammonium sulfamate-phosphate mixture even an exothermic change is observed

A study of the thermal behavior of fabrics when decomposed via the experimental method previously described in Figure 24 of Chapter II shows that the phase and energy changes take place in several distinct steps. When conducted in either nitrogen or $CO_2$ atmosphere, an initial heating period is observed accompanied by evolution of some water and gas during which the fabric is raised to about 300° C. Following this, a rapid reaction proceeds with the usual tar and gas elimination which takes place isothermally. However, in the presence of air, the initial induction period is succeeded by a rapid exothermic reaction, coincident with tar evolution, wherein the fabric temperature rises to from 500 to 700° C. depending upon the velocity of the air supply. The intensity of this spontaneous reaction appears to be independent of variance of the initiating

temperature in the range of 300 to 500° C. Hence, any retardant fun
tioning as an energy absorber or diffuser would be required to mainta
fabric temperatures below 300° C. to prevent continued burning. Follov
ing the tar evolution, the temperature falls for a short time until the resi
ual char begins to undergo the secondary exothermic oxidation whi
coincides with the afterglowing properties of the material. The latter r

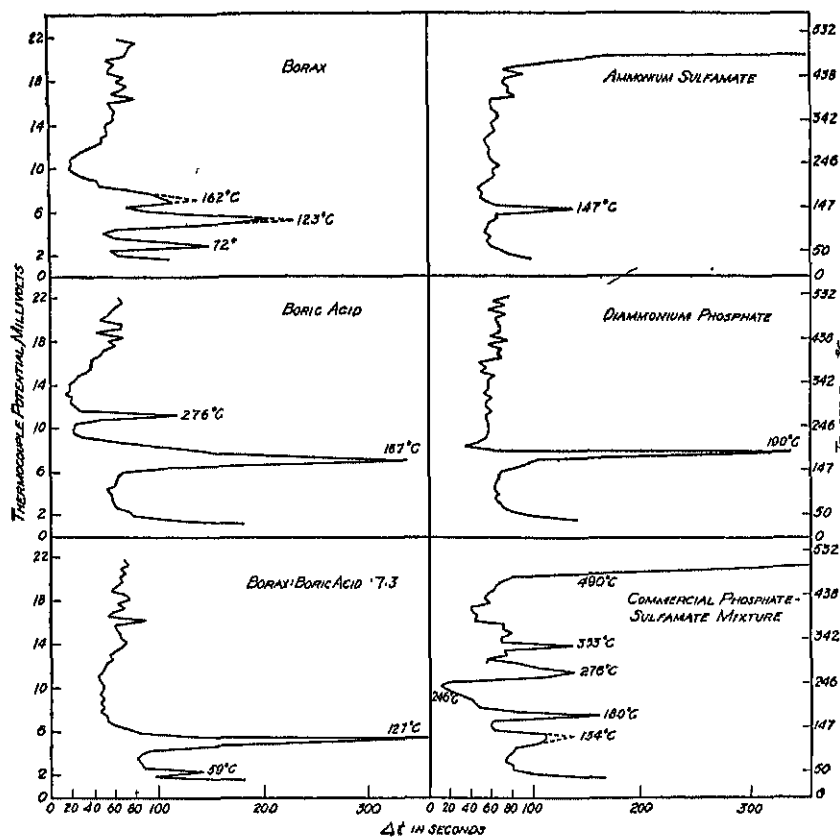



Figure 3. Phase transitions occurring during the heating of various retardants an
the energy changes involved in these transitions.

action, however, is a separate phenomenon and is not pertinent here, bu
is discussed fully in a later chapter. It is the primary dissociation an
oxidation that is directly responsible for the flaming characteristics of th
fabric, and as shown in Figure 4, the intensity and duration of this initia
reaction appear to be unrelated to the good flame-retarding characteristic
of small amounts of the borate mixture. In all cases the initial reactio
proceeds with maximum intensity in the neighborhood of 500° C., and i
is only with excessive amounts that slight physical effects are observed

Similar behavior is exhibited by fabrics treated with other retardants, and no conclusive evidence appears in support of the thermal theories.

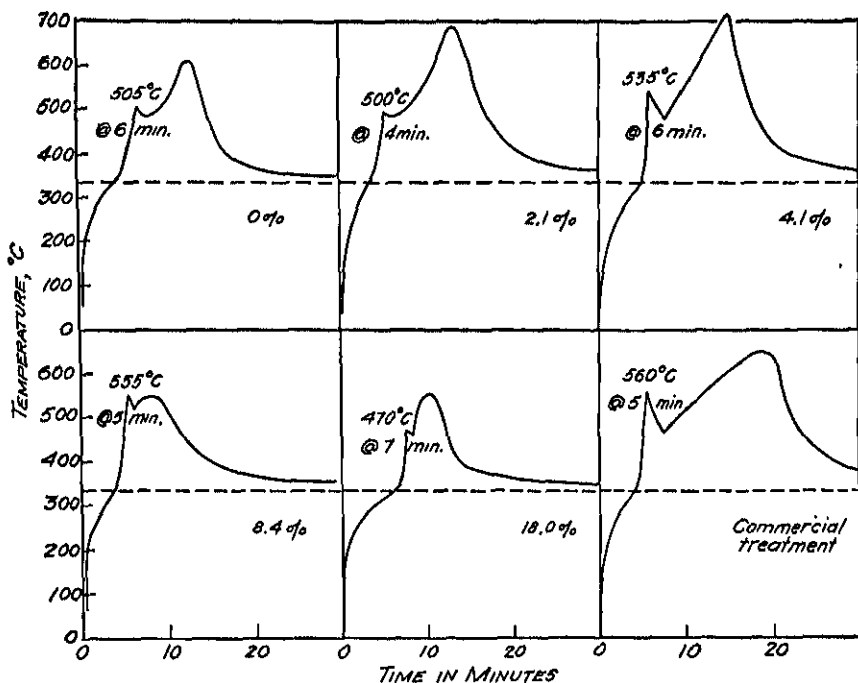



Figure 4. The thermal behavior of fabrics treated with borax-boric acid 1:1 when heated at 330° C. in the presence of air. The per cent values are those added to desized twill and the temperatures are those maxima attained in the primary dissociation reaction.

## B. PREVENTION OF AFTERGLOW

### 1. Chemical Theories

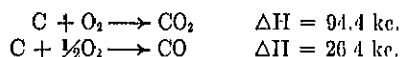
It is apparent that the glowproofing of fabrics is directly concerned with the oxidation of carbon which is the main constituent of the charred residues which undergo this reaction. Studies attempting to elucidate the prime cause for the phenomenon have discouraged investigation due to the limited number of compounds which exhibit good retarding effects. However, some light is cast on the problem by considering those materials which actually enhance the glowing characteristics of cellulose. Here it should be remembered that although such materials as stannic oxide inhibit flaming combustion they render fabric particularly sensitive to consumption by flameless combustion. Similarly, Kramer[15] has found that many metallic oxides have a catalytic action on the oxidation of carbon

[15] Kramer, W. A., "The Catalytic Oxidation of Carbon," Thesis, Ph.D., Ohio State University (1927).

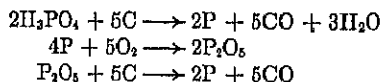
such that the ignition temperature is much lower in their presen burning proceeds much more rapidly. Furthermore, Whitesell and F have shown that although manganese dioxide catalyzes the oxida carbon monoxide, its influence is dependent upon traces of alka when the oxide is prepared free from absorbed alkali the catalytic a on the oxidation is greatly increased. It would appear then that at le enhancement of the glowing characteristics imparted to fabrics metallic oxide type of flameproofing may be attributed to cataly candescent oxidation of carbon following its formation as a cha flame-inhibited cellulose, and that this catalytic activity is ext sensitive to poisoning by alkali.[16]

The above phenomena have direct analogies in the field of glow r tion. Here, as has been shown in Chapter II, although boric ac ammonium phosphate in very small amounts prevent glow, their m with sodium tetraborate are not effective unless the boric acid o phate is in excess. The retardation process is hence likewise susc to poisoning by alkaline salts. The evidence is therefore in favo single catalytic influence on the course of the oxidation of carbon count for both the enhancement and retardation processes.

One of the simplest mechanisms whereby such activity would f appears to be a change in the course of the oxidation favoring a lesser exothermicity than normal.[17] For instance, if the oxidation moted in the direction of CO formation rather than of $CO_2$ formati heat of the reaction is reduced from 94.4 to 26.4 kilocalories per mo

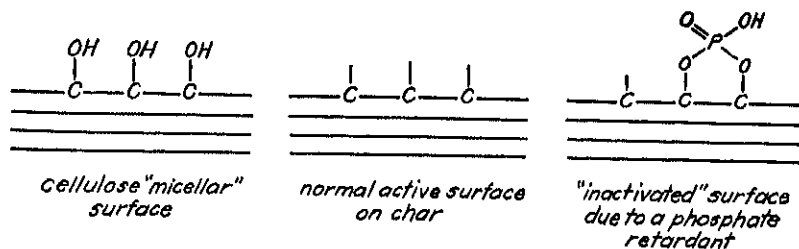
$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = 94.4 \text{ kc.}$$
$$C + \tfrac{1}{2}O_2 \longrightarrow CO \qquad \Delta H = 26.4 \text{ kc.}$$

The inference is then that the first reaction is the self-sustaining g one, while the second, in which the energy change is considerably lo the course taken by glow-retarded fabrics, where the heat liber insufficient to propagate the oxidation after the instigating sourc moved. This theory presumes that the retardants accelerate the for of carbon monoxide and decelerate that of carbon dioxide when c residues are subjected to heat, and is in complete accord with the mentally observed effects given in the previous chapter

The catalytic mechanism favoring the preferred reaction may i changes in energy barriers (heats of activation) for the two reactio may proceed by the following set of reactions:[17]

$$2H_3PO_4 + 5C \longrightarrow 2P + 5CO + 3H_2O$$
$$4P + 5O_2 \longrightarrow 2P_2O_5$$
$$P_2O_5 + 5C \longrightarrow 2P + 5CO$$

[16] Whitesell, W. A., and Fraser, J. C. W., "Manganese Dioxide in the C Oxidation of Carbon Monoxide," *J. Am. Chem. Soc.*, 45, 2841–51 (1923).

[17] Sisson, W. A., Paper presented at Office of Quartermaster General, Con on N.R.C. Project Q.M.C. #27, Washington, D. C. (Dec. 15, 1944).

Here the phosphate directs the carbon to the monoxide form and is regenerated, the net heat liberated in the series of reactions being considerably less than the direct oxidation to the dioxide.

Another possibility is that the active centers on the carbon char may be taken up by the retardant, thus lessening its activity. The surface sorption may be similar chemically to the well-known graphitic acid type such as graphitic bisulfate or fluoride, and the following illustrates a possibility:



*Sketch of fixation of phosphate to cellulose micelle.*

The tenacity with which the glow retardants are held on the char further indicates that the mechanism is associated with a surface catalytic phenomenon, but the data are insufficient to determine the type of sorption involved.

## 2. Physical Theories

The anti-glow properties imparted to carbonaceous residues resulting from the flaming combustion of fabrics have been attributed to a fluid incombustible layer which coats the carbon surface to protect it from direct contact with the oxygen of the air The mechanism is assumed to be identical with a similar theory advanced to account for the inhibition of afterflaming, but suffers in the light of the well-known fact that some retardants have excellent flame- but no glow-retarding influences and vice versa. A typical example is the borax-boric acid system, where the acid protects cotton from afterglow but has little or no effect on the flaming characteristics. On the other hand, borax has a fairly efficient flame-retarding action but shows no flameless combustion inhibiting effects. Mixture of the two materials provides protection from flame but not from glow, despite the fact shown by Ramsbottom and Snoad [1] that the mixtures produce a much better covering and uniformity of coating than the components alone. Similar anomalous behavior is exhibited by the borax-diammonium phosphate system, and it is apparent that the hypothesis falls down upon critical analysis.

In the case of the metallic oxide-chlorinated body system of flameproofing, the latter component is advocated [6] as serving the function of not

only binding the oxide to the fabric but also of inhibiting the glowing tendencies. The coating property of the chlorinated paraffin or resin is assumed either to prevent oxygen infiltration or on decomposition to dilute the ambient oxidizing atmosphere with HCl. Again, these theories are untenable in the light of the facts, since experimentation has shown that even with exceedingly high additions of a wide variety of these chlorinated compounds, with or without metallic oxides, they exhibit no true glowproofing effect. It appears, however, that large amounts of these compounds serve in some measure to reduce slightly the rate at which flameless combustion is propagated in the char and they do actually reduce the tendency for advance of glow into uncharred areas of the fabric. However, they cannot be considered anti-glow reagents in the same sense as the efficient boric and phosphoric acids or substances which produce these two latter materials during contact with the flame.

The further purpose attributed to anti-glow reagents, in that they are assumed to utilize a thermal conduction or insulation function, is likewise not supported by the evidence. When charred fabrics are prepared by pyrolysis in a carbon dioxide atmosphere in the equipment of Figure 2 of Chapter II, and then heated in a stream of air, their thermal behavior may be observed. The rate at which a thermocouple embedded in the char attains a temperature maximum characterizes conductance and oxidation tendencies, and it is found that although all salts retard the rate and extent of temperature elevation, there is little if any correlation between these thermal effects and the glow-retarding properties of the salts, even when these materials are added in large amounts. An example of this type of behavior is illustrated in Figure 5, where effects shown by the excellent glow retardant $NH_4H_2PO_4$ are similar to those exhibited by the good flame- but poor glow-retardant mixture of borax and boric acid in the ratio of 1 : 1. This contrary behavior is further accentuated by the fact that less than 1% of ammonium phosphate will prevent glow in a cleansed fabric, and that additional amounts are unnecessary provided other inorganic substances are absent.

At high temperatures the thermal properties of charred residues from variously treated fabrics are however quite different, and the insulation value of these chars is directly attributable to their glow-resistant qualities. This property is not directly dependent upon the added retardant but is a function of the carbon itself. This is shown by the behavior of fabrics when subjected to various conditions in the equipment in Figure 6, page . Here either flames of a reducing or oxidizing nature or air blasts at various temperatures may be allowed to impinge on fabrics and the resultant temperature at various distances from the opposite face determined. Experimentation shows that flameproofed fabrics, subjected to heat sources of intensity greater than 1000° C. offer resistance to heat transfer so that the ambient temperatures below the fabric are re-

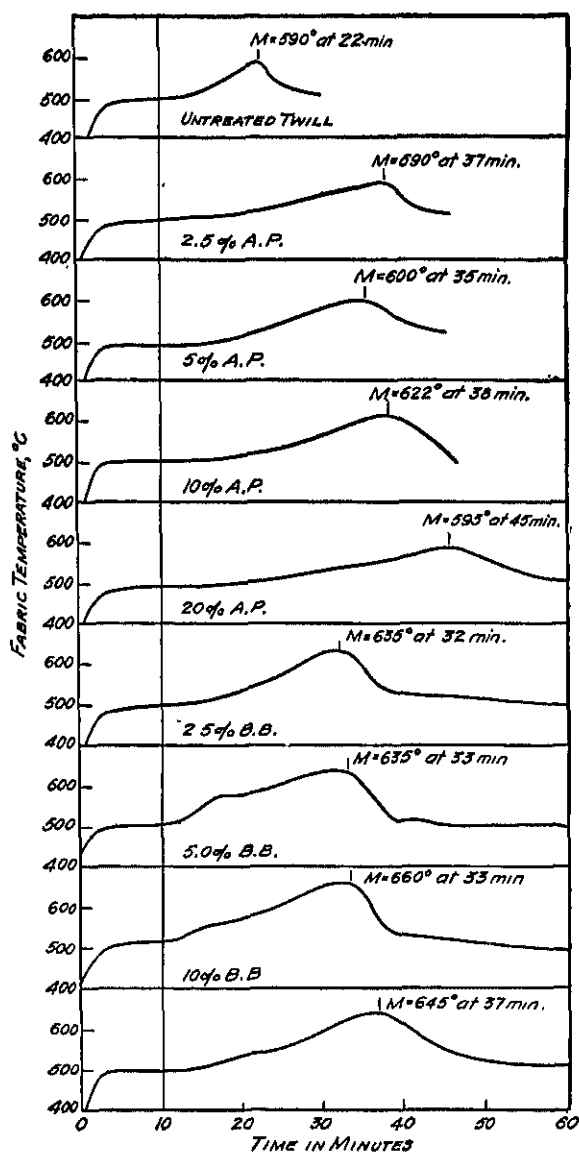



Figure 5. The thermal effects in the oxidation of charred fabrics (Fabrics heated in $CO_2$ atmosphere for 10 minutes, thence in air) The per cent values are the additions of *A.P.* ammonium phosphate, and *B.B* borax-boric acid 1.1. *M* denotes the maximum temperature attained.

considerably, and that glowproofing increases the period over which t protection is effective. This effect is observed irrespective of the natu and intensity of the heat source, since reducing and oxidizing flames well as air blasts from 600 to 1000° C. give similar results. The rate temperatures attained under the glowproofed fabrics compares favoral to that attained with asbestos paper of similar thickness. Similarly, wi air blasts at 800° C., the time required to reach 200° C. at ¼ inch bel

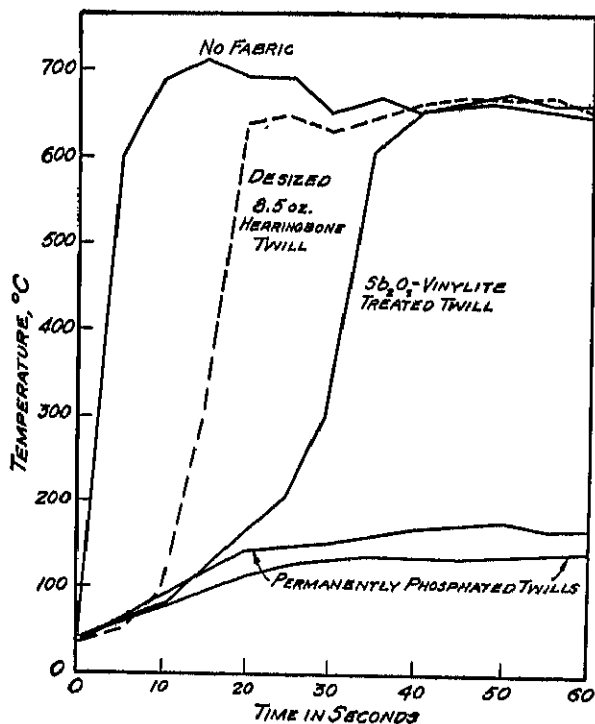
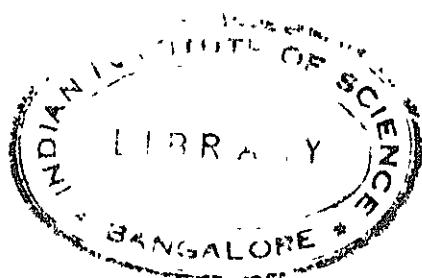
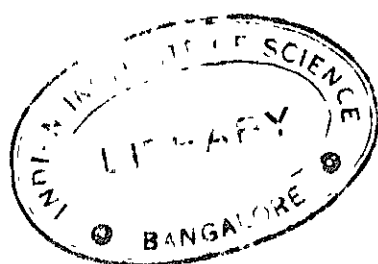



Figure 7. The effect of glow retardation on the insulation afforded by fabrics. The temperatures are those attained in "dead air" ¼ inch behind the fabric, with an ambient external temperature of 600–700° C.

these non-glowing fabrics is equal to or greater than that for glass-asbest or glass-neoprene fabrics either alone or when plied, indicating a high insulating value for the flameproofed cotton fabrics. An example of th behavior of various fabrics is shown in Figure 7. These differences resu from the variance of the type of oxidation pursued by the charred residu With the glowproofed type, the char, retaining all of the fabric-characte of the original material is oxidized slowly and uniformly by the sourc and at no point does it even attain incandescence. The non-glowproofe type, however, attains a white heat and decomposes with rapidity i

various locations allowing for intense radiation, and very soon the cha crumbles allowing the full blast of the incident source to penetrate th material. The insulation is directly dependent upon the retention of a non-penetrable fabric-like structure where the "dead-air" space and the normal low thermal conductivity of carbon function to retard calorific transfer. It is only in an indirect manner that the retardant itself acts in the conductivity barrier via its effect on the type of oxidation pursued by the carbon. In the case of the metallic oxide coatings, however, it appears that the incandescent particles of the flame retardant may contribute to their especially poor insulation effects by enhancing radiation.

The actual physical nature of the carbonaceous residues are not governing factors in their glowing characteristics as shown in the previous chapter, and from the above it would appear unlikely that the glow-retarding phenomena could be induced by the retardant via purely physical means.

## Section Two

# METHODS

# Chapter IV

## Test Methods for Evaluation

An ideal flameproofing agent might be defined as that material which when present in very low add-ons is capable of rendering a fabric completely and permanently resistant to both afterflaming and afterglow without adversely affecting any of the other desirable fabric characteristics. The merit of a flameproofing agent, then, may be considered as being primarily dependent upon its ability to effectively prevent afterflaming and afterglow. Its practical value, however, is also governed by the extent to which it may impair other desirable fabric properties such as hand, strength and the permeability of the cloth to air and moisture vapor. In addition, its practical significance is further dependent upon the permanence of the flameproofness attained as indicated by the resistance of the treated fabric to leaching and laundering and the ionic exchange reactions produced by exposure to excessive perspiration or immersion in sea water. Finally, considering the application to clothing fabrics it is important that the added flameproofing treatment does not increase the heat load imposed by a garment upon the wearer nor produce any other undesirable physiological effects.

In the light of these functional requirements, it is evident that in initiating any experimental program for the investigation of flameproofing agents it is essential that suitable laboratory test methods be available for proper evaluation of the retardants developed and classification as to comparative efficiencies. Any amount of research on new or improved methods of flameproofing will be of little value if the products developed cannot be quantitatively compared with contemporary treatments both with respect to the initial flameproofness achieved and the influences exerted upon other desirable fabric properties. An attempt has been made in this chapter to assemble representative laboratory test procedures as would be required in order to properly evaluate flameproofing agents or treated fabrics. In order to illustrate the significance of the tests described and at the same time outline a suggested program for the comparative evaluation of flameproofing materials, the test procedures are preceded by a description of the performance requirements established for the laboratory investigation of flameproofing agents or flameproofed fabrics.

## A. EVALUATION REQUIREMENTS

*Robert W. Little*

A comprehensive study of the performance characteristics of a flameproofing agent is generally a detailed and time-consuming process. Since, in the course of developing new retardants or evaluating the materials proposed by other investigators, it is often desirable to obtain a rapid initial estimate of the effectiveness of a treatment, the evaluation program employed in the experimental work of N.R.C. Project Q.M.C. #27 included a shorter, less extensive study intended to give a preliminary appraisal of the effectiveness of a retardant. In the event that the material tested demonstrated superior performance in these preliminary experiments, it was then committed to the extensive complete evaluation. The specific tests included in any particular instance are dependent upon whether the material being evaluated is available in the form of the flameproofing agent itself or only as a processed fabric and also upon the expected durability of the retardancy obtained.

Since the flameproofing agents which may be encountered fall rather naturally into the categories of temporary and durable treatments, it is well to consider the evaluation procedure for each of these two cases separately.

### 1. Preliminary Evaluation

#### a. Temporary Treatment

In the event that the flameproofing agent itself is available for evaluation it is desirable to obtain a rough approximation of the minimum add-on requirements for effective flameproofing. To achieve this, two 12 by 20 inch samples are impregnated with add-ons of 10 and 20% by immersion in solutions of these same percentage concentrations followed by squeezing to a 100% wet pickup.

**Flame Tests.** The two samples, treated as described above, are conditioned for at least 24 hours at 70° F. and 65% R.H. and subjected to the 45°-Microburner and Vertical-Bunsen burner flame tests, using duplicate specimens in each case. The flame test data is recorded in terms of afterflame time in seconds, time of afterglow in seconds, and char area or char length in square inches or inches respectively. On the basis of these initial flame tests, the lower effective add-on is selected and employed in the preparation of treated fabric for use in the remainder of the preliminary evaluation tests.

When the material being evaluated is in the form of previously processed fabric, one 12 by 20 inch sample is taken and specimens cut for

duplicate measurements in the 45°-Microburner and Vertical-Bunsen flame tests. In this case the same treated fabric is employed in subsequent evaluation tests.

In order to avoid repetition, references to the "flameproofed fabric" or "treated fabric" in the following discussions will be construed as meaning the treated fabric either as received or as impregnated with the approximate minimum effective add-on previously determined.

**Tendering Tests.** In order to determine the extent of any loss of fabric strength caused by the impregnation process, standard tensile test measurements are carried out on both the untreated and treated fabric. This requires a fabric sample 6 by 12 inches in each case in order to provide triplicate measurements by either the grab or raveled strip tensile tests. Measurements are made in the direction of the warp threads only.

These preliminary tests of a temporary flameproofing treatment afford a rough estimate of its flameproofing efficiency and the effect of the process upon the fabric strength.

### b. Durable Treatments

**Leaching Tests.** In the case of flameproofing treatments of a more or less durable nature, the above evaluation procedure is supplemented by a few simple leaching experiments. The additional specimens required increase the size of the original sample to be impregnated or cut from the treated fabric, whichever the case may be, from 12 by 20 inches to approximately 21 by 23 inches. The initial flame tests are performed as described above for the water-soluble type, employing higher add-ons of 20 and 40% respectively. Again, the lower effective add-on is selected and that fabric employed in subsequent evaluation tests In addition to triplicate tensile strength measurements as performed with the temporary treatments, single 7 by 7 inch specimens of the treated fabric are also subjected to each of the following leaching experiments·

1. 30-minute immersion in distilled water with constant stirring.
2. 5-minute immersion in 5% sodium chloride solution, followed by wringing out excess solution, conditioning 24 hours at 70° F. and 65% R.H. and leaching for 30 minutes in running tap water.
3. 1, 3 and 6 launderings in 0.5% G.I. soap.[1]

Following the leaching and laundering treatments, the specimens are air-dried, conditioned and subjected to the 45°-Microburner flame test, noting the times of afterflame and afterglow and measuring the char area.

These few simple tests provide for a preliminary estimate of the efficiency of a durable-type treatment in terms of its initial flameproofing

[1] The soap listed here and elsewhere in this volume as "G I Soap" is that supplied by the Quartermaster Corps as· Soap, ordinary issue; Specification JCQD No. 1008A, Sept. 17, 1945 (Stock No. 51–S–1644).

characteristics, the effect of the impregnation process upon fabric strength and the resistance of the flameproofness to leaching, ion-exchange and laundering.

## 2. Complete Evaluation

Once a flameproofing treatment has been studied by means of the experiments just described and shown to be fairly effective, it may be considered worthy of more extensive investigation. In this case, the complete evaluation procedure includes a much more detailed survey of the initial flameproof characteristics of the fabric, the variation in fabric strength which may occur and the resistance of the treatment to leaching, laundering and sea water immersion. Furthermore, a study is made of the relative resistances of the treated and untreated fabrics to the passage of moisture vapor and the effects of high temperatures and humidities upon the strength and flameproofness of the treated fabric.

### a. Temporary Treatments

**Flame Tests.** When the flameproofing agent itself is available for study, five 16 by 26 inch samples are treated with add-ons of 5, 10, 15, 20 and 30% respectively by immersion for a 100% wet pickup in solutions of these percentage concentrations. After air-drying and conditioning, the samples are cut into test specimens and tested in quintuplicate using both the 45°-Microburner and Vertical-Bunsen flame tests. On the basis of the flame test performance, a minimum effective add-on is selected and sufficient fabric impregnated with this amount of retardant to serve for the remaining evaluation tests.

Where the flameproofing treatment is available only in the form of treated fabric, one 16 by 26 inch sample is taken and used for quintuplicate measurements in the 45° and vertical flame tests. It is assumed in these cases that the add-on applied to the fabric was close to optimum for the particular process. A sample of treated fabric approximately 30 by 190 inches is required for the remaining tests of a complete evaluation.

**Tendering Tests.** Sextuplicate tensile strength measurements are carried out by means of either the grab or strip test on the treated and untreated fabric and also on the treated fabric after it has been exposed to the following conditions:

1. 2 weeks' storage at 120° F., 85% R.H.
2. 2, 3 and 4 weeks' storage at 150° F., dry.

These accelerated conditions are intended to simulate the extremes which might be encountered in the course of normal use and storage. They were designed primarily for the testing of flameproofed fabrics intended for use in articles of Army clothing.

In addition to these tensile strength measurements, the effect of the tendering conditions upon the flameproof characteristics of the treated fabric is also determined by running triplicate 45°-Microburner flame tests on specimens which have been exposed to 1. and 2. above.

**Moisture Vapor Permeability.** The resistances of both the untreated and treated fabrics to the passage of moisture vapor are determined. This requires nine 4 by 4 inch specimens in order to determine the specific resistances of 1-, 3- and 5-layer assemblies. The intrinsic resistance is calculated in each case and the relative permeability of the treated fabric expressed in terms of the percentage deviation of its intrinsic resistance from that of the untreated material.

### b. Durable Treatments

**Leaching Tests.** With flameproofing treatments which are intended to be of a more or less permanent nature, the above tests are supplemented by rather extensive leaching and laundering experiments. Triplicate 7 by 7 inch specimens of the treated fabric are subjected to each of the following conditions:

1 30-minute immersion in distilled water with continuous stirring.
2 24 hours' immersion in running tap water.
3. 2 hours' rotation in synthetic sea water.
4. 1, 3 and 6 launderings in 0.5% Igepon-T.
5 1, 3 and 6 launderings in 0 5% G I soap.
6. 1, 3 and 6 launderings in 0.5% G I. soap + 0.2% $Na_2CO_3$.

The leached or laundered specimens in each case are air-dried, conditioned for a minimum of 24 hours in the standard atmosphere and tested by means of the 45°-Microburner flame test, notation being made of the usual characteristics of afterflame time, afterglow time and char area.

The complete evaluation procedure outlined in the preceding pages provides a fairly thorough appraisal of the performance of a flameproofing agent as applied to textile fabrics The retardant is classified as to the initial flameproofness produced, the minimum effective add-on required and the effect on permeability characteristics of the fabric Furthermore, an insight is gained into the losses of fabric strength or flameproofness which may result upon exposure of the treated fabric to extremes of temperature or humidity such as might be encountered in the course of use or storage Finally, when the treatment under consideration is of the durable type, the extensive leaching tests indicate the relative resistance of the treatment to solubility and ion-exchange reactions and the degree of alkalinity which the fabric will withstand in laundering solutions.

If a retardant treatment is intended primarily for use in clothing fabrics and, on the basis of the above evaluations appears to very nearly satisfy the requirements for an ideal treatment, additional, more specific

tests may be employed. Included in this group would be the laboratory test for determining the resistance of flameproofed fabrics to excessive perspiration. The final decision as to the suitability of a treatment for use in articles of Army clothing would rest upon the outcome of a series of practical field tests. In these performance experiments, the treated cloth is actually fabricated into garments and worn by men under normal and accelerated conditions simulating those which might be experienced in the course of actual military operations. Wear tests of this type are intended to determine the length of service which a garment may be expected to give, the increase which the added treatment may produce in the heat load imposed by the garment upon the wearer or the nature and extent of any toxic effects which the flameproofing agent may exhibit.

In the following section on test procedures, the tests employed in the laboratory evaluations of flameproofing materials, as well as the supplementary tests suggested, are described in order to define the conditions under which the experimental data presented in later chapters was actually collected. In addition, it is hoped that the presentation of these testing procedures will aid in the standardization of selected methods for use in future investigations of flameproofing materials.

## B. TEST PROCEDURES

### 1. Laboratory Impregnations

*Robert W. Little*

The efficiency of any compound or mixture as a flameproofing agent may be predicted on the basis of its chemical and physical properties and its performance in a number of more or less fundamental laboratory tests. The final decision as to its effectiveness in comparison with known and tested retardants, however, must be based upon practical flame test evaluations of a fabric to which the agent has been applied. It is apparent, therefore, that the method of applying the flameproofing agent to the fabric is of nearly as great importance as the flame test employed in evaluating the treated cloth. The uniformity with which a retardant is applied and the degree of penetration achieved will greatly influence the performance in subsequent tests and hence prejudice the rating which the agent may be assigned in comparison with other flameproofing materials. To obtain a true picture of the relative efficiencies of a group of flameproofing agents, it is imperative that all the members of the group be given an equal chance through a consistent and effective impregnation technique. In the following sections are presented the recommended procedures for the application of flameproofing agents to test fabrics on a laboratory scale. The apparatus is limited to the simplest types of labora-

tory equipment in order to be of help to the greatest number of investigators. Obviously, more uniform and effective applications can be attained through the use of small-scale commercial equipment such as a Butterworth padder. However, the exact nature of the treating apparatus is secondary in importance. The primary requirement is that the same equipment and technique be employed in all cases where comparisons of test data and relative efficiencies are to be made.

### a. Single-Bath Applications

This method of applying flameproofing materials to woven fabrics from a clear solution of the retardant is applicable to those agents which are soluble in organic solvents as well as to the aqueous solutions of the more common water-soluble retardants.

To aid in attaining uniformity of treatment among specimens which are to serve as multiplicates in one of the evaluation tests, a strip of fabric is cut which can be processed as a unit rather than treating each specimen individually and introducing additional variables into the comparisons. Prior to impregnation, the fabric strips are conditioned for at least 24 hours at 70° F. and 65% R.H. and weighed, in order to obtain a control weight of the fabric for accurately determining the add-on obtained. The conditioned strips are then soaked for a total period of approximately 5 minutes in an appropriate volume of the retardant solution of the desired concentration. During the soaking period, the strips are passed twice through a simple hand wringer returning the fabric to the bath each time. The wringer should be set so that the weight of the wet treated fabric is just double that of the untreated strip. This constitutes a 100% pickup and indicates that the treated cloth then contains an amount of retardant expressed in per cent approximately equal to the percentage concentration of the treating bath. The strip of fabric is passed through the wringer a third time and weighed approximately to check on the wet pickup obtained. If the fabric contains too little or too great an amount of retardant, the wringer should be adjusted correspondingly and the reimmersed strip passed again through the rolls. With a little experience, the wringer can be calibrated and accurately set for a 100% wet pickup. The treated strips are finally air-dried and again conditioned for at least 24 hours at the standard atmosphere. A final weighing is made to obtain the apparent dry add-on of the flameproofing agent.

In the case of the temporary type of water-soluble retardants, the treated fabric is now ready to be tested. With some of the more durable treatments, such as the urea-phosphate type, the flameproofing agent is applied from aqueous solution as described above but requires subsequent curing and washing before the fabric is conditioned and weighed to determine the add-on.

### b. Double-Bath Applications

As described above, strips of the fabric to be treated are cut, cond tioned for 24 hours in the standard atmosphere and weighed. The samp strips are then soaked for a period of 5 minutes in an appropriate volu of a solution of the first reactant in the double-bath process, being pass through a hand wringer twice during the soaking period. The samples a then passed between the rolls a third time and weighed to insure a w pickup of approximately 100%. After air-drying, this procedure is r peated using a solution of the second reactant. When several strips fabric are treated simultaneously, a fresh portion of the second soluti should be used for each sample strip. The treated samples are then su jected to a 15-minute leach in running water to remove the unreact water-soluble salts. After conditioning for a period of not less than 2 hours the strips are again weighed to determine the dry add-on obtaine and are ready to be tested.

### c. Suspensions or Emulsions

The prepared impregnating mixture is placed in a V-shaped troug which is held adjacent to a hand wringer and is constructed in such manner that the drippings from the rolls run back into the treating bat A bar or roller at the bottom of the trough serves to hold the fabric in mersed while passing through the bath. Strips of fabric, which have bee conditioned and weighed, are drawn slowly through the retardant mixtu by means of the hand wringer, the rolls of which have been set accordi to the add-on desired. With emulsion and suspension applications it often more desirable to adjust the final add-on by varying the pressu of the wringer rolls rather than changing the concentration of the bat For this reason the desired wet pickup may be other than 100%. In an case, the pressure to be applied in wringing must be determined by ex perimentation and it is well to determine the correctness of the pressu used by weighing the wet strips as they leave the wringer. The strips o fabric are passed through the bath and wringer three consecutive time air-dried to remove the bulk of the volatile organic materials, and finall dried in an oven at 100° C. for 10 minutes to remove the last traces o solvents. After conditioning for a 24-hour period in the standard atmos phere and weighing to determine the dry add-on obtained, the treate fabric is ready to be cut into specimens and tested. The same trough an general method of treatment can be used in the application of resin coat ings to flameproofed fabrics. In this case, however, a single pass throug a dilute resin solution is sufficient.

There are many types of flameproofing agents which require speci

application techniques and cannot be applied by the methods outlined in the preceding sections. In general, however, the majority of the better flame- and glow-retardant treatments may be applied to fabric by one of the techniques described. The fundamentals of these laboratory methods of impregnation closely resemble the type of processes which can be handled on commercial apparatus currently existent in the textile industry. Flameproofing treatments which require very special equipment and techniques for application to the fabric may not be exploited because of the scarcity of special large-scale equipment of a similar nature in the finishing plant.

## 2. Flame Tests

*Robert W. Little*

In any study of the characteristics of flameproofed textiles the flame test employed in evaluating the flame- and glow-resistant characteristics of the fabric is of the utmost importance. The selection of a proper test procedure must be based upon a careful consideration of the type of fabric being used, the nature of the flame exposure to which it may be subjected in the course of service, and the requirements as to flameproofness which the treated fabric is expected to meet.

It is essential that the investigator be aware of just what property of the treated fabric he is desirous of evaluating. In the case of treated fabrics which are flame resistant, but might not be classified as truly flameproofed, the characteristic to be measured may be the inflammability or ease of ignition. It may be, on the other hand, that the most interesting property is not the ease of ignition, but rather the rate at which the fabric burns once ignition has been accomplished This might be termed combustibility. With efficiently treated materials the property to be tested would be the general flameproofness of the fabric. The requirements of a test for quantitatively determining relative flameproofness, inflammability or combustibility would be very different in each case.

Considering the flame tests commonly employed in the testing of flameproofed fabrics, the observations recorded serve to estimate the degradation suffered by the specimen through three different mechanisms. The char area or char length measurement serves as an index of the total damage suffered by the fabric, while in contact with the igniting flame and also resulting from extended afterflaming or afterglow. The time of afterflaming in seconds is a measure of the extent of decomposition caused by autocombustion after the igniting flame has been extinguished. Finally, the duration of afterglow serves as an estimate of the damage suffered through oxidation of the charred residue and adjacent fabric once all flaming has ceased Which of these flameproof characteristics is considered to be the most important will largely govern the selection of a proper

flame test and will be dependent upon the end use and performance requirements of the fabric being considered. It cannot be emphasized too strongly that the selection of the proper test apparatus and procedure is dependent upon the anticipated use of the fabric and the requirements to be satisfied. A flame test which is too severe or too mild may give an entirely erroneous picture of the relative efficiencies of flameproofing agents for a specific application.

A great number of laboratory burning tests have been developed for estimating the relative flame and glow resistance of flameproofed fabrics. For a complete picture of the tests developed and the details of their manipulation the reader is referred to the technical, trade, and patent literature on the subject.[2, 3] An attempt will be made in the following pages to present a brief outline of the best of the available tests, emphasizing those which show special merit and appear to be most widely applicable.

## a. Tests for Relative Inflammability

Under the pressure of current legislation in the state of California and impending federal legislation, this test has recently been developed by a special subcommittee of the American Association of Textile Chemists and Colorists. This committee on Flammability of Consumer Textiles was charged with the responsibility of developing a test method and apparatus which would serve to measure the relative inflammabilities of consumer fabrics and hence afford a means of differentiation between hazardous and non-hazardous fabrics. The definition of a given flaming time in seconds as signifying a dangerously inflammable fabric is obviously a difficult and responsible task and one which would require the careful comparison of test data obtained cooperatively by many different operators. This correlation work is still in progress and hence the final details of the test method and performance requirements have not yet been stated The test is unique at the present time, however, and warrants presentation as far as the details have been established. It is readily apparent that a test of this type would not be applicable to the testing of truly flameproofed fabrics. It is primarily intended as a means of differentiating between various untreated fabrics, classifying them as somewhat hazardous or highly hazardous based upon their burning characteristics.

**A.A.T.C.C. Flammability Test.** The apparatus as it now stands is shown in Figure 1. It has been developed to be completely automatic, eliminating nearly all the personal error attributable to the operator. The specimen rack is adjustable in order to compensate for the differences in

[2] "The Fireproofing of Textiles." Research Rept. of Textile Research Institute, Inc. (July, 1943).

[3] "Recommended Requirements for Flameproofing of Textiles." National Fire Protection Assoc., Boston, Mass. (1941).

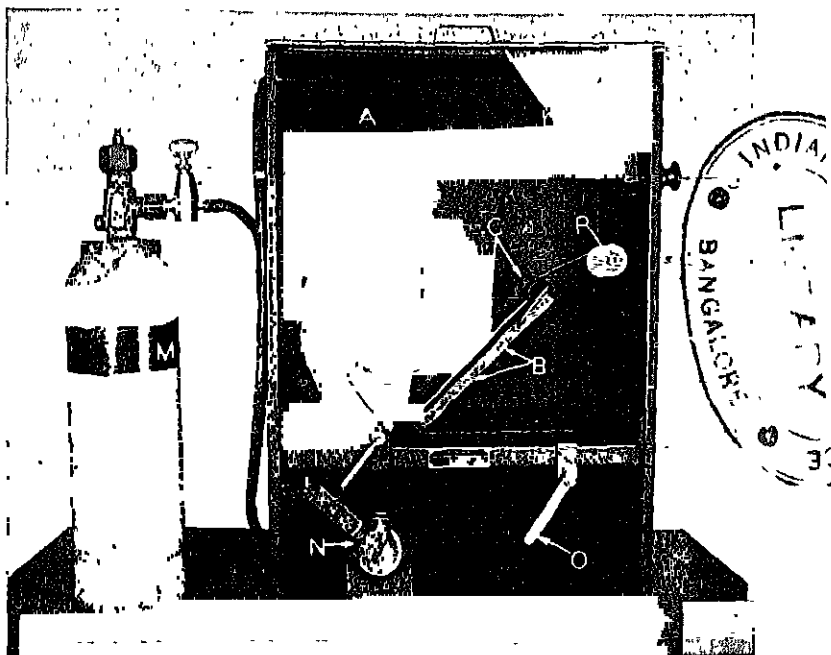
fabric thickness. A specimen shield is provided to hold the test specimen flat on the rack and prevent curling once flaming begins. The shield at the same time eliminates any possible edge effects by covering the cut edges of the specimen.

*Courtesy of American Association of Textile Chemists and Colorists.*

Figure 1 A.A.T.C.C. Flammability Tester

*A*. Draft-proof chamber with adjustable top.

*B*. Specimen rack, fixed at an angle of 45°, consisting of a 4 by 7 inch framework laced horizontally with heat-transmitting wire.

*C*. Specimen shield which covers all but a 1.5 by 6 inch strip of the test specimen

*D*. Indicating finger, by means of which the thickness of the sample is compensated for in the throw of the gas nozzle.

*F* Gas nozzle.

*G*. Stop cord which determines vertical flame height.

*H*. Guide for stop cord.

*I*. Stop weight, clipped to cord.

*J*. Control for holding sliding door open

*K*. Slide door (shown in end view) normally slides in the grooves at the front of the cabinet

*L*. Fuel control valve (used in conjunction with a flowmeter).

*M*. C.P. Butane container.

*N*. Stop watch and timing mechanism

*O*. Starting lever.

*P*. Cord supply.

Quintuplicate specimens, 2 by 6 inches, are cut from the fabric being tested, 5 being cut parallel to the warp threads and 5 parallel to the filling. These are dried in an oven for 15 minutes at 105° C. and cooled in a desiccator for at least 3 minutes. The desiccator contains anhydrous cal-

cium chloride along with cobalt chloride to indicate the efficiency of the desiccant. Specimens are tested immediately upon removal from the desiccator and the data recorded as to the time in seconds which elapses from the moment the flame contacts the fabric until the apex of the flame reaches a plane horizontal to the top edge of the specimen. Bringing the starting lever over to the extreme right and releasing it starts the timing mechanism which applies the flame to the fabric for the 1-second period of exposure. The timing is automatically recorded by the watch, starting when the flame first contacts the specimen and stopping when the flame reaches and burns the fine thread across the top of the specimen.

Just what flaming time is to be considered as the demarkation line between acceptable and dangerous fabrics will necessarily be dependent upon the outcome of the extensive correlations now in progress.

### b. Tests for Relative Combustibility

Still considering treated fabrics which are flame resistant but do not possess sufficient flame retardancy to prevent combustion once ignition has been accomplished, tests have been developed to determine the relative burning rates of fabrics. This type of test is a valuable tool in the more fundamental studies of flameproofing agents. It enables one to make close comparisons between the relative efficiencies of various treatments by studying the burning characteristics of low add-on fabrics. The sensitivity of the test is such that the effect of sizing alone on the burning rate of the fabric may be clearly indicated.

**Flame-Rate Test.** This test for measuring the rate of flame propagation of a burning fabric was developed in the course of the experimental work of the flameproofing project at Columbia University under N R C Project Q.M.C. #27. No special apparatus is required for carrying out the test though a convenient cabinet could easily be designed

A 2 by 30 inch strip of the fabric to be tested is marked off in 5-inch intervals and suspended from a wire by means of small metal clips placed at 2.5-inch intervals along the entire length of the specimen. The wire is held taut at an angle of 30° to the horizontal and the fabric surface lies in a vertical plane. The entire apparatus must be enclosed in a draft-proof hood. The fabric is well ignited at the lower end by means of a match or Bunsen burner and notation made of the time required for the flame to travel each 5-inch interval. The time is not recorded for the first interval since burning begins erratically and becomes steady during this period. Similarly, the time for the last 5-inch interval is not very dependable since the burning often becomes erratic at the end of the strip. By plotting length in inches against time in seconds and taking the slope of the line, the burning rate of the fabric is expressed in terms of inches per second.

It is convenient to cut the test strips parallel to the filling threads though

specimens may be taken with warp or filling as long as they are cut consistently in the same direction of the fabric. In some cases where one surface of the cloth varies radically from the other, as with the brushed pile type of fabric, it is desirable to suspend the test specimen with the fabric surface in a horizontal plane. This is readily accomplished by supporting the strip between two parallel wires. A convenient method of attaching the fabric to the wires is by means of an office stapling machine. The wire staples are driven loosely into the edge of the strip such that one arm of the staple clamps into the fabric and the other arm remains free to be threaded on the supporting wire. The versatility of the test is enhanced by the ability to vary the angle of inclination of the test strip. When interested primarily in fabrics of very low combustibility the specimen may be inclined at an angle approaching the vertical. With highly combustible fabrics, on the other hand, the test strip may be inclined at angles only slightly removed from horizontal. Obviously, for any given set of comparative tests, the angle of inclination should be held constant.

Q.M.C. Flammability Test.[4] This test as employed at the Philadelphia Quartermaster Depot requires a test specimen 1 by 6 inches.

The apparatus consists of two metal frames resembling miniature ladders which are hinged together at their upper ends and supported from a ring stand at an angle of 30° to the horizontal. The frames are 8 inches by 1.25 inches, the cross rods being 1.5-inch lengths of No. 28 heat-resistant wire.

The specimen is clamped between the two frames with 0.25 inch of the lower end hanging down from the frame end. Ignition is accomplished by holding a safety book match to this lower end for 5 seconds. Notation is made of the time required to burn the 6-inch strip including the 5-second ignition period. In the event that the specimen is not consumed, the length of the charred area is taken as the measure of "flammability." The results are expressed in the following manner:

"N" seconds or

"Supports combustion," extinguished after "N" seconds; "x" char length or

"Does not support combustion"; "x" char length.

This test does not provide the sensitive differentiation of the foregoing test but is convenient for some applications. In general the use of supporting wires across the test specimen introduces inconsistencies into the results due to the heat taken up by the wires themselves.

### c. Tests for Relative Flameproofness

A great many different flame tests have been developed for determining the relative efficiencies of flameproofed fabrics. The tests differ from one

[4] "Test Methods for Textiles." P.Q.D. No. 447A (Jan. 19, 1945).

another with respect to the test cabinet, size of sample, alignment of t test specimen, nature of the heat source, duration of exposure of the he to the fabric and the observations recorded. Some of the available te are valuable for certain specific uses but are not generally applicable the over-all problem of flameproofness. Others are almost universally a plicable to the testing of flameproofed fabrics but do not emphasize c

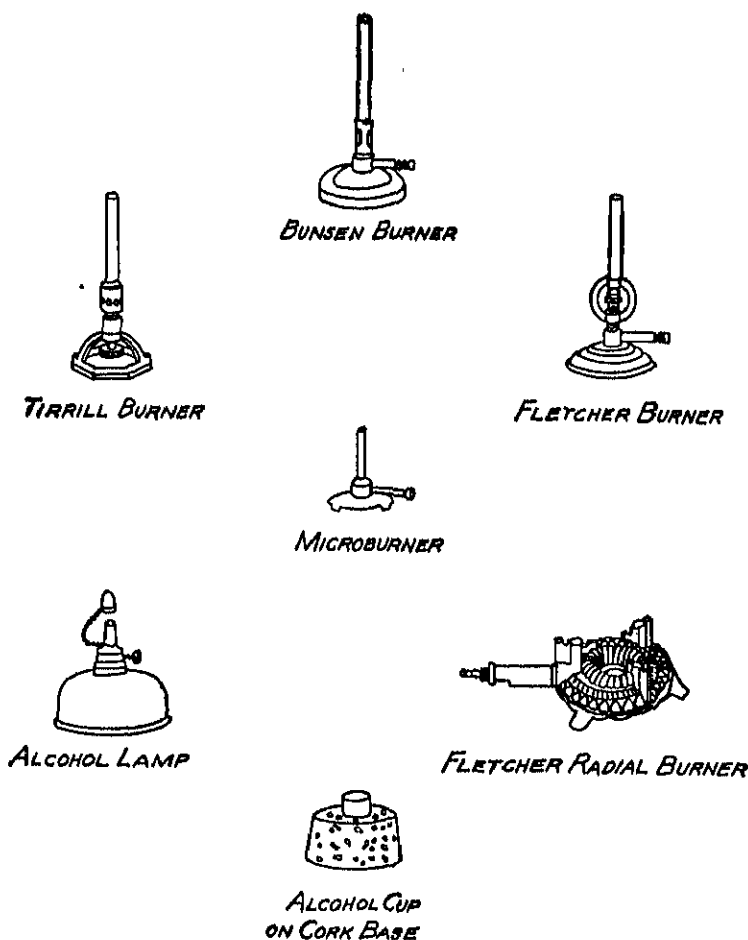



Figure 2. Various flame sources employed in tests for relative flameproofness

characteristic sufficiently to be desirable for very specific applications. few of the better-known flame tests, which are representative of the se eral types, are presented in the following pages. A brief description apparatus and technique has been given in each case. With the more less standard tests the reader is referred to the literature cited for the c tails which have been omitted. To assist in describing the means of igniti

in the several tests, the more common flame sources are presented pictorially in Figure 2.

### (1) *Vertical Specimens*

**Underwriters' "Flammability" Test.**[5] The apparatus consists of a sheet iron stack, 12 inches square and 7 feet high which stands on legs 1 foot off the floor. The test specimen, which is 7 feet long by 5 inches wide, is hung from a bar at the top of the tube such that its bottom edge is 5.75 inches above the top of a 0.375-inch Fletcher burner. The burner flame is adjusted to a height of 11 inches by varying the air intake, maintaining a gas pressure of 108 mm. of water. The specimen is exposed to the flame for a 2-minute period and the time of ignition and time of cessation of flaming and glowing recorded. Also a measurement is made of the distance from the tip of the flame to the top of the charred area.

The test as described has several limitations. The test specimen is not held securely in place during the test and hence moves about as flaming progresses. The test is by necessity limited in its applicability as a research instrument because of the space required to house the apparatus and the amount of material required for the test specimens.

**Freeman Stove Pipe Test.**[6] The apparatus in this case consists of a 5-inch brass tube, 24 inches long, which is lined with asbestos paper. The tube is ventilated by means of eight 0 75 by 1.50 inch vertical slots at the bottom. Six 24 by 3 inch specimens are tested simultaneously by hanging them at regular intervals from a rack at the top of the tube. Ignition is accomplished by burning 1 oz. of excelsior inside the base. Relative performance is based upon the per cent of the initial weight lost.

A modification of this test has also been proposed[4] in which the igniting flame is that of a 5-inch radial Fletcher burner adjusted to a height of 4 inches. In the modified test only three specimens are tested at one time and the exposure time is reduced to 15 seconds.

Due to the severity of the conditions of this type of test, most flameproofed fabrics are almost completely destroyed and thus there is little opportunity for differentiation between various treatments. In addition the deterioration in terms of per cent loss in weight depends too much upon the weight and weave of the fabric used

**Vertical-Bunsen Burner Test.** The test cabinet consists of a sheet-metal shield 12 inches wide, 12 inches deep and 30 inches high, open at the top and provided with a vertical sliding glass door. A space is left at the bottom of the front to permit manipulation of the gas burner used in igniting the specimen.

[5] "Recommended Requirements for Flameproofing of Textiles." Nat'l. Fire Protection Assoc., Boston, Mass. (1941).

[6] *Trans. Am. Soc. Mech. Engr.*, 27, 71 (1906).

With each sample of flameproofed fabric, ten 2 by 12.5 inch specim
are cut for test, five with their long dimension in the direction of the w
and five in the direction of the filling. The specimen being tested is
pended vertically from the top of the cabinet by means of a clamp wl
covers the upper 0.5 inch of the length. The lower edge of the speci
is adjusted to be 0.75 inch above the top of a Bunsen or Tirrill gas bur
The burner has a tube of 0.375-inch inside diameter and the flame hei
is regulated to 1.5 inches with the air supply completely shut off.
resulting flame is luminous and wavering.

The flame is applied vertically in the middle of the lower end of
specimen for 12 seconds, then withdrawn and the duration of afterflam
in seconds is noted. The specimen remains in place in the cabinet for
duration of any afterglow and the length of the charred portion is t
measured. This is accomplished by inserting hooks in the lower port
of the specimen, one on each side of the charred area, supporting a gi
weight on one hook and slowly raising the other. The char length is defi
as the distance from the lower edge of the specimen to the extremity
the tear produced.

The criteria of an effectively flameproofed fabric by this test are t
the specimen shall not show more than 2 seconds' afterflaming, the aver
length of char of the ten specimens shall not exceed 3.5 inches, and
maximum length of char for any one specimen shall not be greater t
4.5 inches.

This test is quite widely used and, with minor differences, is the
employed by the U. S. Bureau of Standards,[7] the National Fire Protect
Association,[5] U. S. Government Agencies,[8, 9, 10] American Society for Te
ing Materials,[11] and the National Research Council of Canada.[12]
cabinet specified by the Bureau of Standards is 14 inches wide rather th
12. As employed at the Philadelphia Quartermaster Depot, the appara
includes a sample holder which clamps the specimen preventing curl
and wavering during the test. In addition, the specimens are removed fr
the test cabinet when afterflaming has ceased and hung on a special v
rack throughout the afterglow period. Both the cabinet and the afterg
rack are kept in a draft-proof hood. The method and apparatus of
Canadian National Research Council differ from the above method

[7] "Flameproofing of Textiles" S. B Detweiler, Jr.—Letter Circular No. 4(
Nat'l. Bur. St'ds. (1936).

[8] Duck, Cotton; Fire, Water and Weather Resistant Fed Spec CCC-D-
(Feb. 17, 1939).

[9] "Test Methods for Textiles." P.Q.D No. 447A (Jan 19, 1945).

[10] Quartermaster Corps, Tent. Spec.—J Q.D. No 242 (Dec. 2, 1942).

[11] "Tentative Specifications for Fire-Retardant Properties of Treated Te
Fabrics." A.S T.M. Standards on Textile Materials.

[12] "Schedule of Methods of Testing Textiles." Canadian Gov't. Purchasing Sta
ards Comm.—No. 4-GP-2-1942 (Oct. 15, 1940). Amended Jan. 16, 1942.

two important particulars. The cabinet does not have a glass door on the front, both the top and front being open. Furthermore, in addition to the afterflaming time and char length, attention is paid to the occurrence of any flashing of the sample upon contact with the flame and the time of afterglow is measured.

The Vertical-Bunsen test possesses many advantages, among them being the simplicity of operation, small specimen required and the small flame which helps in attaining reproducibility. It also, however, suffers from several disadvantages, some of which can be obviated rather easily.

In the early work of the N.R.C.–Q.M.C. Flameproofing Project at Columbia University, a Flame Test Cabinet was developed in which vertical, horizontal and 45° flame tests could be carried out (see Figure 3). In adjusting the Vertical-Bunsen test to this cabinet as a research instrument for use on flame-proofed clothing fabrics, several of the previous disadvantages were avoided. A small pilot light was attached to the burner which provided instantaneous ignition and more accurate timing of the ignition period. Furthermore, it eliminated the necessity of moving the burner into position each time. The burner was fixed permanently in position in the cabinet which greatly improved reproducibility As an additional aid in maintaining a constant adjustment of specimen and burner, the lower corners of the test strip were anchored to the floor of the cabinet by means of rubber bands or light wire springs. These could be easily clipped on the fabric and held it quite firmly in position without excess tension on the specimen. The cabinet itself was covered on top leaving a ventilation hood, and the opening at the front was replaced by a series of 0.5-inch holes along the bottom of each side. This provided adequate ventilation but avoided undesirable drafts. The extremely wavery luminous Bunsen flame necessitated reducing the open spaces in the cabinet in so far as possible. All test specimens were conditioned for at least 24 hours in the standard atmosphere of 70° F. and 65% R.H. and it is believed that this should be one of the required steps in all flame test procedures. Since the clothing fabrics being tested were generally efficiently flameproofed, the specimens were allowed to remain in the test cabinet throughout the afterglow period. This has been found to lead to more consistent and dependable data whether the actual time of afterglow is considered or not In the belief that afterglow occurring in the clothing could be equally as dangerous as afterflaming and much more difficult to extinguish, the time of afterglow in seconds was observed along with the afterflaming time and length of char. The criteria of flameproofness assigned to the Columbia tests were that the treated fabric exhibit no afterflaming, less than 4 seconds' afterglow, and a char length not greater than 3.5 inches. These requirements as to the performance of the specimen in the flame test are obviously dependent upon the weight of the fabric, the type of treatment desired, and the use for which the fabric is intended.

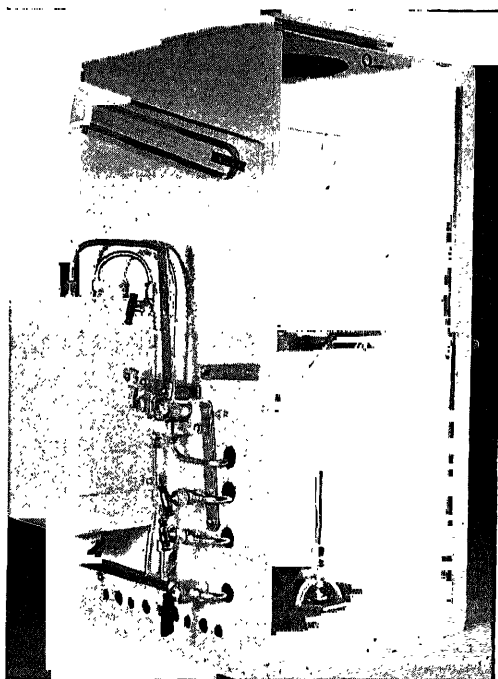
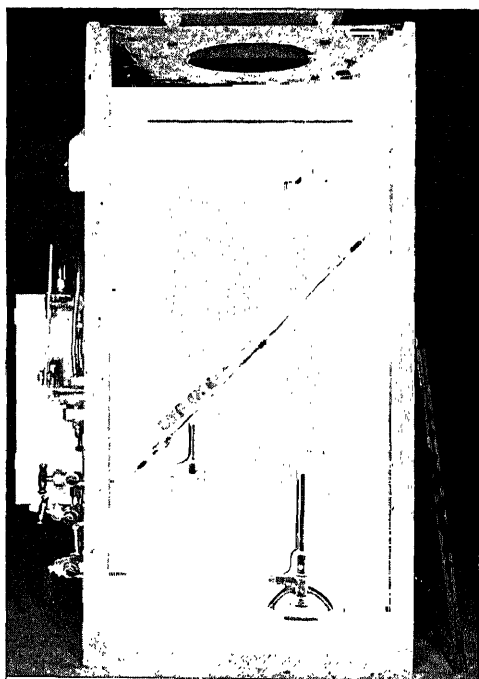
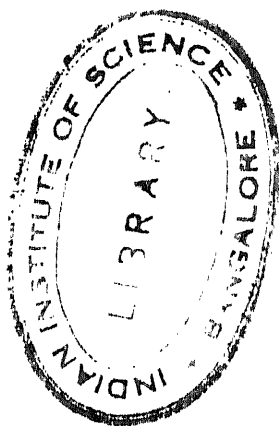



Figure 3. Columbia Flame Test Cabinet.

A. Side view, showing pyrex-glass doors in place, control valves and reservoir-manometer system for maintaining constant gas pressure.



B. Front view with sliding doors removed showing vertical and 45° test specimens in position for testing.

In comparison with 45° and horizontal tests, the alignment of the test specimen in the vertical direction produces those test conditions which are the most severe with respect to afterglow. Many treated fabrics which display no afterglow in the horizontal or 45° tests show a relatively strong afterglow when subjected to the vertical test. In contrast, the Vertical-Bunsen test shows the least tendency towards afterflaming when testing efficiently flameproofed fabrics. It is therefore apparent that, though it may have universal applicability, the Vertical-Bunsen burner flame test is of particular value in those cases where afterglow is the flameproof characteristic of primary interest.

### (2) *Horizontal Specimens*

**Corps of Engineers—"Flame-Resistance" Test.**[18] No specific test apparatus is described in the specification though it is stated that "the test shall be conducted in a hood or enclosed space so that the test shall not be affected by drafts."

Two 9 by 6 inch specimens of the impregnated fabric are conditioned for not less than 24 hours in the standard atmosphere and immediately tested. By means of a testing frame (which is not described) the specimen is supported in a horizontal position with the center of the specimen 3 inches above the lip of the cup containing the fuel. The igniting flame is obtained by burning 0.3 ml. of anhydrous ethyl alcohol (absolute) in a flat-bottomed brass cup. The brass cup is constructed of 1/32-inch sheet stock and is 11/16 inch in outside diameter and 9/32 inch high. A material of low heat conductivity such as cork is used as a base for the test cup. The test specimen remains in position until afterglow has ceased. Without removing the specimen from the testing frame the charred area of the fabric is removed by punching a hole in the char and running a pencil around the inside of the hole with slight pressure on the sides. A measurement is then made of the longest dimension of the resulting hole. The requirement of flame resistance is that the average size of the burned hole shall not exceed 2.5 inches.

Apparently no attention is paid to the duration of either afterflaming or afterglow. The test was designed for a specific purpose and is limited in its applicability.

**Horizontal-Microburner Test.** In designing the cabinet for the testing of flameproofed fabrics under the Columbia University flameproofing project, a rack was designed which enabled the use of horizontal specimens and the microburner flame. In the photographs of the Columbia Flame Test Cabinet shown in Figure 3, the supporting strips for the horizontal rack can be seen along the sides of the cabinet in Figure 3–B.

[18] Corps of Engineers, Tentative Specification—"Compound, Flame Resistant, Emulsifiable, for Fabrics." E.B.P. No. 674 (June 29, 1944).

Both the apparatus and test procedure for this test are identical with those of the 45°-Microburner test described in the following section, the only differences being the use of a different supporting rack to hold the specimen frame and the placing of the specimen such that the flame impinges on the center of the test piece.

Placing the specimen in a horizontal position produces test conditions which are the most severe with respect to afterflaming. The prevention of the removal of combustible decomposition products by any natural draft greatly intensifies the tendency of the fabric to flame after the igniting flame has been extinguished. In many instances fabrics which exhibit no afterflaming tendencies in the vertical and 45° tests show several seconds' afterflaming when tested horizontally. This test, therefore, is much more sensitive to minor differences in afterflaming tendencies and would be preferable for those applications where the flameproof characteristic of primary interest is the relative resistance of the treated fabrics to afterflaming. The tendency of fabrics to afterglow when tested horizontally is not nearly as great as in the case of the 45° and vertical tests. For this reason, in cases where the resistance to afterglow is felt to be of primary interest or equal in importance to the afterflaming tendencies, the horizontal test would be less desirable than one of the other two.

### *(3) 45° Specimens*

**British Standards Institution Test.**[14] The apparatus consists of a wire grid which is stretched on a 6.5-inch square metal frame and rested on vertical supports at an angle of 45 degrees. The igniting flame is produced by burning 0.3 ml. of absolute ethyl alcohol in a small metal cup. The cup is identical with that previously described under the horizontal test of the Corps of Engineers. In this case, the cup is supported on a cork such that the center of its base is 1 inch vertically below the center of the lower fabric surface.

A 6 by 6 inch specimen is spread over the wire grid and exposed to the alcohol flame which generally lasts for 45 to 50 seconds. A record is made of the afterflaming and afterglow times following the extinction of the igniting flame and the extent of the char is measured. The requirement for a well-treated fabric is that it shall not char for a length greater than 2 inches.

**Canadian Surface Burning Test.**[12] This is essentially an improved modification of the British Standards Institution Test. The apparatus and procedures are essentially the same as those described above with the following modifications:

The test specimen is 6 by 7 inches and is fastened to a metal frame such that a 6 by 6 inch surface is exposed. The sample is clamped at the

[14] British Standards Specification 476 (1932).

four corners and is in contact with the metal frame on only two sides. The entire 6 by 6 inch square is open to the flame and is not in contact with a wire screen. Furthermore, the test is carried out in a three-sided sheet metal screen, 10 inches wide, 10 inches deep, and 32 inches high, thus affording some protection from drafts. Three specimens are cut from each sample to be tested and classified according to the afterflaming time, afterglow time, and char dimensions under one of the three following categories: non-inflammable materials, materials of very low inflammability, and materials of low inflammability. It should be noted here that afterglow which is confined to the charred area is disregarded in this test.

**45°-Microburner Test.** The Flame Test Cabinet developed by the personnel of N.R.C. Project Q.M.C. #27 at Columbia University is pictured in Figure 3. The wooden cabinet is 12 inches wide, 12 inches deep, and approximately 25 inches high by inside dimensions. The front of the cabinet is completely closed by means of two vertical-sliding pyrex glass doors. Ventilation is afforded by means of the 0.5-inch holes along the bottom of each side and the 6-inch hooded vent in the top. The microburner is securely fastened to a square wooden block which is set in a fixed position in the cabinet. Notched metal strips screwed to the sides of the cabinet serve to keep the specimen racks in constant alignment with the burner. Two sets of these strips are used, one to support the rack for the 45°-Microburner test and the other for the shorter rack of the horizontal test as described earlier in this section. The gas to be supplied to the microburner is held at a nearly constant pressure by means of the reservoir shown. The water manometer indicates the relative gas pressure and when at an angle of 15° to the horizontal is maintained at approximately 22 mm. A small pilot light is permanently attached to the microburner and avoids moving the heat source once the specimen is in position for test.

Three identical specimens are prepared for each measurement, being conditioned for at least 24 hours at 70° F./65% R.H. before testing. A 7 by 7 inch test specimen is placed smooth side up in a 5.5-inch square metal sample holder similar to an embroidery frame. The sample is placed at an angle of 45° in the metal rack which is positioned so that the lower part of the fabric directly above the microburner is 0.75 inch above the top of the burner. The center of the burner is 1 inch horizontally from the edge of the lower metal strip holding the sample. The microburner flame, previously adjusted with a slight yellow tip to a height of 1.75 inches by means of the needle valve in the gas supply line, is applied to the smooth side of the fabric near the lower edge for a period of 12 seconds. The specimen remains in position in the cabinet throughout the afterglow period. The data recorded include the duration of afterflaming and afterglow in seconds and the charred area as measured with a planimeter.

Investigation has shown that, for all practical purposes, it is immaterial

whether the flame burns in the direction of the warp threads, in the direction of the fill threads, or at 45° to both as shown in the illustrations. It has recently been found, however, that the charred area can be most consistently measured by tearing the charred portion similarly to the practice in the Vertical-Bunsen test. This is accomplished by cutting a small cross in the char directly above the burner and carefully tearing the char, once in the direction of the filling and once parallel to the warp threads, pulling against a standard weight hooked into the fabric. The torn charred area is then defined by connecting the four extremities of the tears using a soft red pencil and following the general shape of the total darkened area. When the torn charred area is to be measured, the specimen should be aligned in the cabinet so that the flame burns in the direction of either the warp or the filling.

The Columbia Test Cabinet incorporates several advantageous features which afford a simpler and more reproducible test procedure and also tend to give a greater degree of precision in flame test measurements. The addition of pilot lights avoids the use of matches or other methods of ignition and leads to more accurate timing of the ignition period. In addition, the sample and burner are in constant alignment which contributes greatly to the reproducibility of data. The closed cabinet is practically draftless and yet possesses good visibility and adequate ventilation to insure a good supply of air. The reservoir and manometer system on the gas-inlet line to the microburner could undoubtedly be improved upon but some similar measure should be taken to insure a fairly constant gas supply to the burner. The entire apparatus is compact and in one piece permitting it to be moved from one place to another without requiring extensive readjustment.

The microburner flame has many advantages over the luminous Bunsen flame. Being non-luminous, the flame of the microburner burns much more steadily and vigorously and is not affected by slight drafts. The Bunsen flame, in contrast, wavers with any air current and may be blown completely away from the test specimen by a moderate draft. The temperature of the microburner flame at the point of contact with the fabric is quite constant remaining at 823 ± 11° C. over a period of weeks. This will be dependent of course upon the uniformity of the particular gas supply used. The temperatures of the two flames are actually very similar at the point 0.75 inch above the top of the burner as illustrated in Figure 4.

It has been pointed out previously that the flame tests in which the specimen is aligned in a vertical position are the most severe with respect to afterglow. Similarly, placing the test specimen in a horizontal position tends to intensify the afterflaming tendency of the fabric. As might be expected, fabrics tested by means of a 45° test exhibit afterflaming tendencies midway between the vertical and horizontal tests and afterglow tendencies more severe than the horizontal test but not as extreme as when suspended vertically. Consequently, in choosing a flame test for universal

applicability, wherein the characteristics of afterflaming and afterglow are weighted equally in importance, it would be advisable to use the 45° compromise which does not exaggerate either the flaming or glowing tendencies. If, for a particular application, the resistance to afterflaming is the characteristic of major importance, the 45° test should be supplemented by measurements using the horizontal test. If the afterglow is of

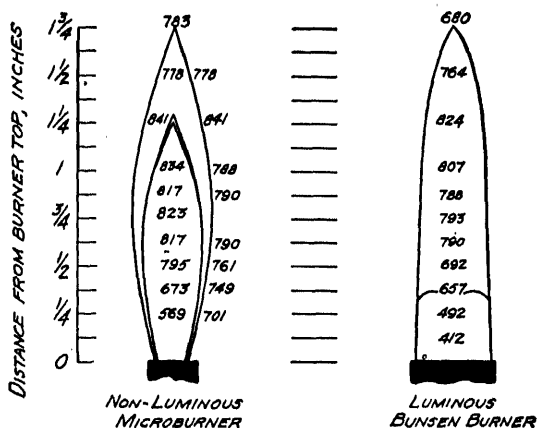



Figure 4. Comparative temperatures of Microburner and Bunsen burner flames as employed in standard flame tests.

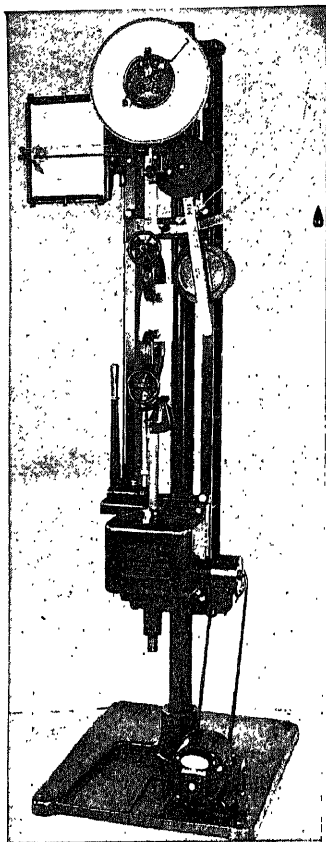
major importance and the afterflaming a secondary requirement, the 45° test should be supplemented by parallel determinations with the vertical test. Regardless of the requirements to be met, considerable experimental data have clearly shown that the 45° test produces much better reproducibility and allows a wider differentiation between the relative efficiencies of comparable flameproofing treatments.

### 3. Fabric Strength

*Robert W. Little*

Of primary importance in the evaluation of a flameproofing treatment or flameproofed fabric is the measurement of the effect which the treatment has upon the strength characteristics of the cloth. A retardant treatment, regardless of its efficiency in the prevention of afterflaming and afterglow, would be quite unsatisfactory for any practical application if, in the course of the treatment or use of the treated fabric, the strength was seriously impaired so as to render the fabric unserviceable. For this reason, the tensile and tear strengths of the fabric are generally determined before and after the application of the flameproofing treatment and also after exposure of the treated material to surveillance and permanence tests.

The selection of a test apparatus and procedure to be employed is rela-

tively simple since these techniques for studying the load-elongation relationships of fabrics have been carefully standardized and universally accepted. The reader is referred to standard specifications of these tests

*Courtesy of Scott Testers, Inc., Providence, R. I.* *Courtesy of Alfred Suter, New York, N. Y.*

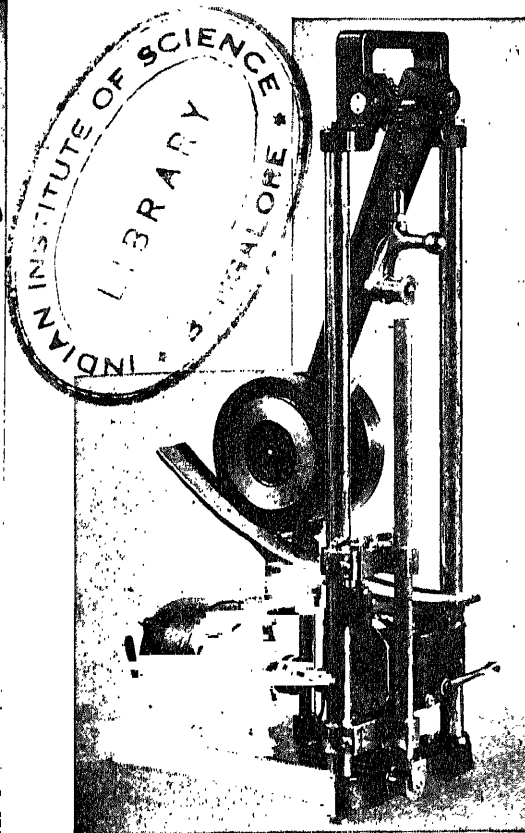



Figure 5. Pendulum type tensile testing machines.

(*left*) Scott Model J showing fabric clamps and autographic recorder.
(*right*) Suter tester equipped with skein rollers. These may be replaced by fabric clamps and an autographic recorder can be attached.

for the details which may be omitted from the following discussions.[15,16]

Of the two general types of textile testing machines for the determination of the breaking strength and elongation of textiles,[17] *i.e.*, the pendulum

[15] A.S.T.M. Standards on Textile Materials (1944).

[16] Textiles, General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. IV, Part 5—CCC–T–191a (April, 1937).

[17] Standard Specifications for Textile Testing Machines—A.S.T.M. Designation D76–42.

type and the constant specimen-rate-of-load type, the former is perhaps more widely used and will be considered in this discussion. Typical examples of the industrial machines available are the Scott and Suter Testers shown in Figure 5. Several different models of this type of instrument are available, varying in capacity and design, in many cases having been developed for a specific fiber or fabric.

The strength characteristics of a fabric which are of major interest are the breaking strength, the elongation and the tear strength.

### a. Breaking Strength

**Grab Method.** The distance between the clamps at the start of the test is exactly 3 inches. The face of one jaw is 1 by 1 inch square and that of the other jaw 1 by 2 inches or more, with the longer dimension perpendicular to the direction of application of the load.

The test specimens are cut 4 inches in width and not less than 6 inches in length. Quintuplicate specimens are used for determining warp breaking strength which have the longer dimension parallel to the warp yarns. An equal number are cut with the longer dimension parallel to the filling threads for determining the filling strength.

The specimens are placed symmetrically in the clamps with the longer dimension parallel to the direction of application of the load, care being taken to see that the same yarns are gripped in both clamps. The average of the five individual specimens shall be reported as the warp or filling breaking strength. Individual results which fall appreciably below the average are discarded as are the results of tests in which a jaw break or slippage is apparent.

**Raveled-Strip Method.** With the following exceptions, this test is carried out in the same manner as described for the grab test:

The faces of the jaws, in this case, measure 1 by 1.5 inches or more, the longer dimension being perpendicular to the direction of application of the load. Test specimens are cut 1.25 or 1.5 inches in width, depending upon the number of threads per inch, and raveled to a width of exactly 1 inch by removing approximately the same number of threads from each side.

**Cut-Strip Method.** This test is performed just as described for the Raveled-Strip test with the exception that the specimens are cut to a width of 1 inch rather than cutting wider and raveling to that width. The test is applicable to those coated or impregnated fabrics which would be difficult or impossible to ravel.

### b. Elongation

Using testing machines as described above, which include an autographic recording device, the elongation of the fabric can be determined

at the same time that the breaking strength measurement is made. The elongation at any stated load can be obtained from the graph and the average of the five specimens expressed as elongation in terms of percentage increase in length.

### c. Tearing Strength

**Tongue Method.** Using the same machine as described for the method for breaking strength, the pawls of the pendulum are disengaged from the ratchet.

Quintuplicate specimens, 3 inches in width and at least 8 inches in length, are cut in both the warp and filling directions. A 3-inch longitudinal cut is made from the center of one of the short edges and running lengthwise of the specimen. One of the tongues is placed in each clamp of the tester and, by means of the autographic recording device, a measurement made of the average load necessary to tear the fabric. The warp and filling tearing strengths are reported in the form of the average of the five individual tests.

**Trapezoid Method.** The machine is again the same as that used for the grab breaking strength measurement with the exceptions that the faces of the clamps are 1 by 3 inches or more, with the long dimension perpendicular to the direction of the load, and the distance between the clamps at the start of the test is 1 inch. Again, the pawls of the pendulum are disengaged from the ratchet.

Quintuplicate specimens, 3 inches in width and 6 inches in length, are cut in the directions of both warp and filling threads. An isosceles trapezoid is marked on each specimen having an altitude of 3 inches and bases 1 and 4 inches in length. A 0.25-inch cut is made in the center of the 1-inch edge and perpendicular to it. The specimen is clamped in the machine along the non-parallel sides of the trapezoid with the cut halfway between the clamps, the short edge taut and the long edge lying in folds. The average load necessary to tear the fabric is obtained by means of the autographic recording device. The warp tearing strength and filling tearing strength are calculated as the average of the five individual tests in each case.

The various types of flameproofing treatments exert quite different effects upon the strength characteristics of the fabric. In some cases the breaking strength is seriously impaired with only a relatively slight decrease in tear strength. Those treatments which tend to produce a film or coating on the fabric, on the other hand, do not reduce the breaking strength but generally cause a marked decrease in tearing strength. Which of the fabric strength measurements assumes the greatest importance depends to an appreciable extent upon the future use for which the treated fabric is intended.

## 4. Leaching Tests

*Rogers B. Finch, Allan J. McQuade, and Robert W. Little*

### a. Laboratory Tests

In the development work on flameproofing treatments of a more or less durable nature, it is often desirable to employ a rapid and simple laboratory test to obtain an initial estimate of the permanence of the treatment. In the event that the flameproofing constituents withstand these mild leaching conditions they may then be considered of a durable type and evaluated further by means of the more severe laundering and sea water tests which follow.

**Static Water Leach.** A 7 by 7 inch specimen of the treated fabric is conditioned for 24 hours at 70° F. and 65% R.H. and weighed. It is then sewn to a 6 by 6 inch rectangular stirrer frame made of glass rod and immersed in approximately 4 liters of distilled water in a 4-liter beaker. The stirrer is rotated for 1 hour at room temperature at a rate of approximately 40 R.P.M. After removal from the beaker and frame, the specimen is air-dried, reconditioned in the standard atmosphere and re-weighed to determine any loss of retardant. The specimen is finally tested by means of the 45°-Microburner flame test.

This mild leaching is concerned with removal by a dissolving action only since the use of distilled water avoids any possible exchange and the slow stirring exerts almost no mechanical flexing on the fabric.

**Running Water Leach.** Two methods used in evaluating fire-resistant treated fabrics are described in this section. The first method was developed for use under N.R.C. Project Q.M.C. #27 at Columbia University. A 7 by 7 inch specimen of the fabric is conditioned and weighed. It is then immersed in a round-bottomed trough of approximately 1-gallon capacity into which tap water is introduced at such a rate as to produce marked turbulence. The water is introduced at the bottom of the tank and exits at the top, producing a tumbling action. The specimen is tumbled in this running water for a period of 24 hours, air-dried and reconditioned. The fabric is then weighed to determine the loss of flameproofing agent and its flameproofness checked with the 45°-Microburner Test.

The exposure of some treatments to such large quantities of tap water will produce some loss of flameproofness due to ion-exchange. This will vary with the hardness of water used. In addition, the mechanical action occurring in the tumbling of the specimen may cause some impairment of retardancy though this should not be appreciable.

The second method is used at the Jeffersonville Quartermaster Depot for the leaching of fire-resistant duck for tentage. There, in order to

accommodate the large number of samples received daily for both inspection and development purposes, a tank 42 inches in length, 19 inches wide, and 21 inches deep is employed. This tank is divided lengthwise into three parts to produce along each side a compartment 2 inches wide parallel to the length. The center portion, 15 by 42 inches, is further partitioned across its length into 40 cells approximately 1 inch in width, thus providing a separate compartment for each sample to be tested and avoiding the possibility of contamination. Water is piped to the center of the tank and enters one of the narrow sections parallel to the length of the tank. By means of slots the flow of water is then directed to the top of each sample compartment. At the bottom of each compartment and on the opposite side from the inlet the water is directed into the third section which runs parallel to the length of the tank. A waste pipe is placed in the center of this section at a level slightly below that of the inlet to draw off the flow of water. The inflow water pipe is jacketed to allow it to be heated by steam, the introduction of which is thermostatically controlled to insure water of 70° F. temperature.

Thus this leaching tank provides a means for a constant flow of water of even temperature to be directed down and across each sample which hangs vertically in an individual compartment free from contamination of materials removed from other samples.

In the conduct of the test two fabric samples each 12.5 by 10 inches in size are selected, one with the longer dimension parallel to the warp and the other parallel to the filling. Each is suspended below the water level in separate compartments, and the water flow is regulated to provide at least six complete changes of water during each 24-hour period. Upon completion of the desired leaching period, generally for 72- or 168-hour periods, the fabric samples are removed and air-dried before exposure to standard conditions. Each sample is then cut into five 2.5 by 10 inch specimens to allow fire-resistance determinations to be made using the Vertical-Bunsen test.

On the whole, fair results were experienced with this method and those fabrics which had water-soluble fire retardants were quickly discovered. In addition, when fabrics leached for 168 hours in this tank were examined for mildew resistance the results gave a good indication of the mildew resistance of the same fabric after 4 to 6 months' outdoor exposure in Jeffersonville.

**Spray Leaching.** Leaching of fire-resistant tentage fabrics at Jeffersonville was also carried out in a Model X–1A Accelerated Weathering Unit manufactured by the National Carbon Company.[18] In this machine a circular rack 37.5 inches in diameter revolves within an enclosed drum at such a speed as to provide one complete revolution for each two-hour

[18] For details of the equipment and operating procedure, see paragraphs 5b and 5b(2), Section IV, U. S. Army Spec. No. 100–48 (May 11, 1945); also see Section 9 of this chapter.

period of machine operation. Located within the revolving rack a spray nozzle is provided to impinge water in a conical spray upon samples carried by the revolving rack. In the center of the machine is a carbon arc enclosed with Corex D filter panels. To provide artificial light, Sunshine type carbons are employed and maintained at constant amperage across the arc. Thus, during each revolution the samples are exposed to the spray for approximately a ten-minute period, and the remaining time to light. The period of exposure to such conditions is generally 200 hours, and for some comparative tests it has been extended to 400 and 600 hours.

In the conduct of the test two fabric samples each 12.5 by 11 inches in size are selected, one with the 11-inch dimension parallel to the warp and the other sample with its 11-inch length parallel to the filling. The samples are positioned upon the revolving rack with the 11-inch dimension in a vertical plane and are attached solely to its top portion. Upon completion of the desired exposure period, the fabric samples are removed and air-dried for a 24-hour period before exposure to standard conditions. The unexposed portion of the sample, 1 by 12.5 inches in size, is removed and the remaining fabric divided into five specimens each 2.5 by 10 inches. These are used for fire-resistance tests employing the Vertical-Bunsen method. It was also the practice to apply the flame to that 2.5-inch edge which had been in the lowest position during the test.

This test method provides a much better indication of the fire-resistance retention of tentage duck than did the tank method previously outlined, and in addition a fair estimation of the color change to result in field tests is obtained. However, in both these respects it is not as severe as that which occurred in field tests. As would be expected where a large quantity of tap water of considerable hardness is employed, one type of finish was markedly impaired due to ion-exchange reactions. Such a condition has not been fully confirmed upon actual outdoor leaching.

### b. Field Tests

Outdoor exposure of tentage fabrics is performed on the grounds of the Jeffersonville Quartermaster Depot with the sample mounted at a 45° angle, facing south.[19] A specimen 42 by 30 inches with its longer dimension parallel to the warp is mounted on fiber board using large copper tacks spaced 6 inches apart. In some cases the fabric is supported on all four sides, providing no backing agent. In this manner one side is exposed to the weather for periods up to one year.

In nearly all instances the fabric samples were mounted on the fiber board since this produced a more severe condition and the tensile strength losses sustained were more in keeping with those experienced in other localities. In addition, it represented a use comparable to that which occurred in the life of paulins.

[19] Paragraph 3, Section XIII, Federal Spec. CCC-T-191a (April 23, 1937).

Due to the fact that Jeffersonville is located in an atmosphere in which industrial gases prevail, especially during the winter months, it was necessary that only those exposures which were initiated about April 1 and continuing for a six months' period be considered as somewhat indicative of the effectiveness of the treatment. Lastly, to allow comparison between various types of treatments it became necessary to standardize on two types of base grey fabric, which were 12.29-ounce Army duck and 11.6-ounce tent twill.

The significance of these tests in comparison with laboratory evaluations is discussed in Chapter VII, Section A–2–b.

### 5. Laundering Tests

*Robert W. Little*

Since the durable types of flameproofing treatments are intended for an initial treatment without the necessity of reprocessing, they must be capable of withstanding normal laundering conditions. A test procedure is required, therefore, to evaluate in the laboratory the resistance of flameproofed fabrics to laundering. The retention of flame and glow resistance on laundering will be greatly dependent upon the washing procedure employed and the nature of the detergent solution. For this reason it is necessary to adhere to a more or less empirical test method in order to achieve any degree of reproducibility.

Several standard laundering tests have been developed for determining the color fastness of dyed fabrics. The official methods of the United States Government,[20] the American Association of Textile Chemists and Colorists,[21] and the American Society for Testing Materials [22] are very similar in nature and with minor modifications are applicable for use in testing the permanence of flameproofed fabrics. In the case of the color fastness tests, several separate procedures are given using different constituents in the wash solution and varying bath temperatures and the length of the washing period. In adapting the techniques for use with flame-retardant fabrics a single washing procedure was employed, the severity of the laundering being varied only with respect to the detergent mixture employed.

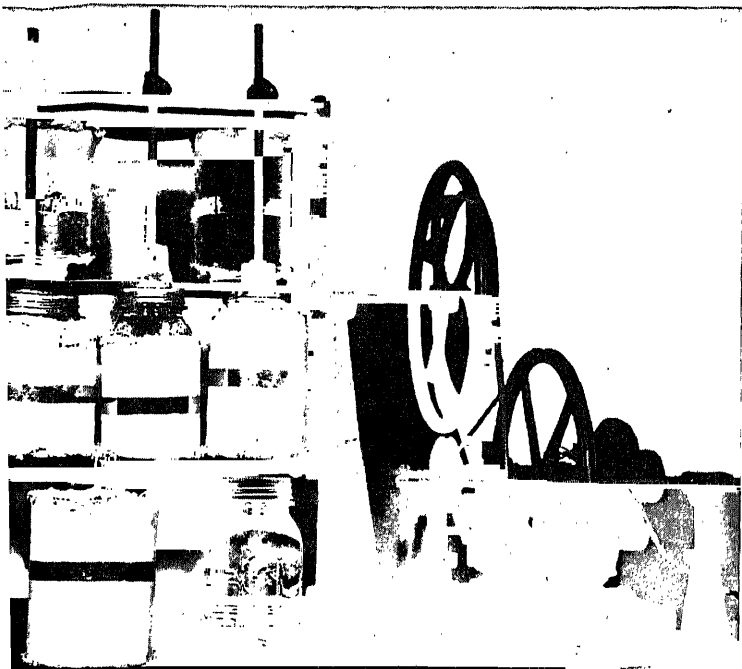
A second type of laundering test which could be used for the evaluation of flameproofed fabrics is that now commonly employed in determining shrinkage in laundering.[20,23] This method employs a large specimen, 20

[20] Paragraph XIII–4, Textiles, General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. IV, Part 5—CCC–T–191a (April, 1937).

[21] A.A.T.C.C. Official Method C–1–42 (No. 3)—Standard A.A.T.C.C. Test Methods, 1943 Yearbook.

[22] A.S.T.M. Designation: D435–42 (No. 3); A.S.T.M. Standards on Textile Materials (1944).

[23] A.S.T.M. Designation D437–36; A.S.T.M. Standards on Textile Materials (1944).

s or larger, and the washing is carried out in a small reversing of the cylindrical type. A test of this sort might more nearly e the conditions existing in commercial laundry practices. tory comparisons of the relative permanence of flameproofing however, where it is often desirable to test several different simultaneously, the first mentioned tests appear to be better The individual specimen jars permit the washing of many dif- ated specimens without any chance of contaminating one fab- products leached from another.

ratory rotator employed as a launderometer in the early experiments of N.R.C. Project Q.M.C. #27.

ering tests carried out in the course of the flameproofing lumbia University were performed in two types of launder- t. One washing procedure was developed making use of a tator which would accommodate jars of one-quart capacity. eries of tests were carried out in the A.A.T.C.C. standard r. The apparatus and procedure of both tests are presented ng pages in order to be of assistance to those who may not Launder-Ometer available but do have a laboratory rotator adapted to accommodate one-quart jars.

r **Launderometer.** The complete apparatus employed is ure 6. The rotator consists of a cast iron frame capable of

holding six 1-quart Mason jars. The jars are clamped, three on each side of the frame, such that the jars on opposite sides are also at the opposite ends of the rotating holder. The horizontal shaft of the machine is 0.5 inch above the plane of the jar cap and is displaced 2 inches from the vertical axis of the jar. Thus the jars in revolving effectively rotate about an axis approximately 2 inches above the center of their covers. The Mason jars are encased in asbestos jackets and clamped in the rotator which turns at the rate of 15 R.P.M.

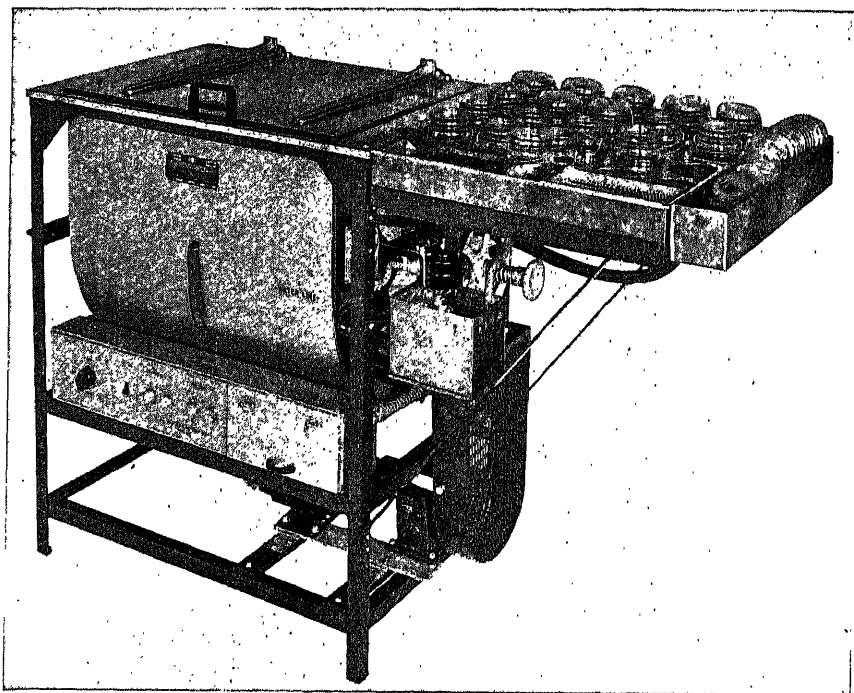
The procedure used is very similar to that described in Federal Specifications.[20] A single specimen is placed in a 1-quart Mason-type jar along

*Courtesy of Atlas Electric Devices Co., Chicago, Ill.*

Figure 7. Atlas Launder-Ometer, Model LHD-EF.

with twenty 0.75-inch glass marbles. 400 cc. of the soap solution, which has been heated to 160° F., is added to the preheated jar, the jar sealed and rotated for 30 minutes. The soap solution is then poured off, replaced by 400 cc. of water at 160° F., and the jar rotated for 10 minutes. The specimen is rinsed once more by rotating for 10 minutes in a fresh 400-cc. portion of water at 160° F., and finally by rinses of 3 minutes each in an 0.05% acetic acid solution at room temperature, and in cold water. The rinsed specimen is hung to dry under room conditions.

**Atlas Launder-Ometer.** The fully automatic, electrically operated machine, including the preheated loading table, is shown in Figure 7.

A detailed description of the apparatus and the process of its development can be obtained from the literature.[24] The use of a specially designed instrument of this type has many advantages particularly when a great number of tests are being made. The automatic temperature regulation of the bath and preheating table plus the compactness and ready availability of the items required reduces greatly the tedium of routine tests. The machine consists essentially of a large copper tank containing a rotor capable of holding twenty standard pint jars. The rotor is driven at a standard speed of 42 R.P.M. The jars, covers, rubbers and test balls are all preheated to the operating temperature in the tray shown by means of circulating the water from the laundering chamber.

The laundering procedure in this case is very similar to that of test No. 3 of A.S.T.M.[22] and A.A.T.C.C.[21] A single test specimen is placed in a 1-pint Mason-type jar along with ten 0.25-inch steel balls. A 100-cc. portion of soap solution, previously heated to 160° F., is added and the jar rotated for 45 minutes at that temperature. The soap solution is then poured off and the specimen subjected to two consecutive 1-minute rinses in 100 cc. of water at 105° F. The fabric is then soured by agitating for 2 minutes in 100 cc. of 0.05% acetic acid solution at room temperature followed by a 2-minute rinse in 100 cc. of cold water. The rinsed specimen is hung to dry under room conditions.

The A.A.T.C.C. launderometer can be obtained with a special rotor to accommodate 1-quart jars. This is desirable in view of the size of specimen required for the 45°-Microburner flame test. In that case the volumes of solutions used would be increased to those given for the laboratory launderometer method.

In the laundering tests carried out under the N.R.C.–Q.M.C. Flameproofing Project, three different soap solutions were employed:

Solution 1 — 0.5% Igepon-T.
Solution 2 — 0.5% ordinary issue G.I. soap.
Solution 3 — 0.5% G.I. soap + 0.2% $Na_2CO_3$.

These were intended to represent the varying degrees of severity which might be encountered in the course of military or commercial launderings. Since the launderings are intended primarily for use in comparative studies it is not necessary to duplicate exactly all of the conditions which may be encountered in actual usage.

Although the two techniques described above are quite different in several respects, extensive laboratory comparisons have shown that they are nearly equal in their effect upon the flameproof characteristics of the fabrics tested. This is illustrated by the data of Table 1, comparing the flameproofness of three different fabrics after laundering according to both

[24] *Am. Dyestuff Rep.*, p. 697 (Oct. 29, 1928).

sary in evaluating military clothing fabrics which might well be exposed to more or less prolonged immersion in sea water in the course of amphibious landing operations. It is also probable, moreover, that flameproofed duck used for tarpaulins or deck covers might well be exposed to a similar leaching action on exposure to sea air and spray. The test is more universal, however, since it is concerned with the resistance of flameproofing compositions to an exchange reaction with alkali and alkaline-earth ions whether brought about by sea water immersion, saturation with perspiration or leaching or laundering in hard water. The treatments primarily concerned with these base exchange reactions are those of the urea-phosphate type. The influence exerted by alkali and alkaline-earth ions upon the salts of cellulose esters has been previously discussed. The pigment-type emulsion and suspension treatments are not seriously affected by sea water immersion though in some cases the resistance to afterglow is somewhat impaired.

In the course of the experimental work of the Flameproofing Project at Columbia University, it was necessary to develop an apparatus and procedure for carrying out this test. The only available comparable tests, those commonly employed in estimating the fastness of dyes to perspiration and sea water, were entirely unsuitable for the purpose.

The apparatus consists of a standard laboratory rotator in which cylindrical, wide-mouthed jars of 1-pint capacity are rotated at a speed of approximately 12 R.P.M. about an axis parallel to the diameter of the jars.

The synthetic "ocean water" is prepared in the form of two stock solutions and diluted for use as required. The compositions of the stock solutions, according to the formulae of Lyman and Fleming,[25] are as follows:

*Stock Solution #1*

| *Material* | *Grams* |
|---|---|
| $NaCl$ | 1878. |
| $Na_2SO_4$ | 313.4 |
| $KCl$ | 53.1 |
| $NaHCO_3$ | 15.4 |
| $KBr$ | 7.7 |
| $H_3BO_3$ | 2.1 |
| $NaF$ | 0.24 |
| $Na_2SiO_3$ (40%) | 3.4 |
| $H_2O$ | 7000. |

*Stock Solution #2*

| *Material* | *Grams* |
|---|---|
| $MgCl_2 \cdot 6H_2O$ | 851.9 |
| $CaCl_2$ | 88.2 |
| $SrCl_2 \cdot 6H_2O$ | 3.2 |
| $H_2O$ | 800. |

A volume of 195 cc. of solution #1 is diluted with water to a total volume of 1 liter. Similarly, 35 cc. of solution #2 is diluted up to 1 liter with water. The two liters are then mixed and the resulting solution used in the tests.

[25] "The Oceans," Sverdrup, Johnson, and Fleming, Prentice Hall, Inc. (1943).

Six identical specimens of fabric, 7 by 7 inches square, are cut f
test. A specimen is placed in each of the jars along with 250 cc.
water" and rotated for the required time at 70° F. The specimen
removed from the jar, blotted between cotton toweling to remove
solution, and air-dried. After conditioning the specimens for at l
hours at 70° F. and 65% R.H., they are tested for flameproofness by
of the 45°-Microburner flame test.

One specimen of the group, in each case, is subjected to rotation
sea water for a period of 15, 30, 60, 90 and 120 minutes. The sixth sp
is tested as a control. The results are expressed in terms of "Resist
Sea Water," which may be defined as the time in minutes which a
proofed fabric may be rotated in the "ocean water" solution witho
nificantly affecting the flameproof qualities of that fabric. In the
military clothing fabrics it was required that the resistance to sea
be at least 120 minutes.

## 7. Perspiration Resistance

*Robert W. Little*

The measurement of the resistance of flameproofed fabrics to the
of perspiration is a test intended specifically for use with clothing f
The property evaluated is similar to that determined by means of t
Water Resistance Test previously described but the latter is consid
more severe in its leaching action.

The most satisfactory method of determining the deleterious ac
perspiration upon flameproofed clothing fabrics would naturally
series of heat load experiments in which the treated garments are a
exposed to the sweat of human subjects under controlled wearin
ditions. Experiments of this type have been conducted and the m
used will be discussed in a later section. In the majority of cases, ho
it is either impractical or impossible to carry out extensive progr
this type. It is therefore desirable to develop a simple accelerated l
tory test which approximates as closely as possible the conditions e
tered by the fabric in the course of the heat load experiments.

The only available tests for determining the resistance of text
perspiration were those employed in measuring the fastness of dye
conditions of those tests were thought to be too mild for the purp
mind. The test procedure which follows was developed by the staff
Flameproofing Project at Columbia University in an attempt to p
a simple laboratory test which would simulate the life of a garment
under severe wearing conditions.

The test apparatus presented diagrammatically in Figure 8 cons
a closed cabinet with a glass front which is maintained at a tempe
approximating that of the body (30° C.). The fabric specimens ar

pended on a wire frame which may be slowly rotated. The synthetic perspiration solution is introduced into the cabinet in the form of a very fine spray by means of an air-powered spray gun.

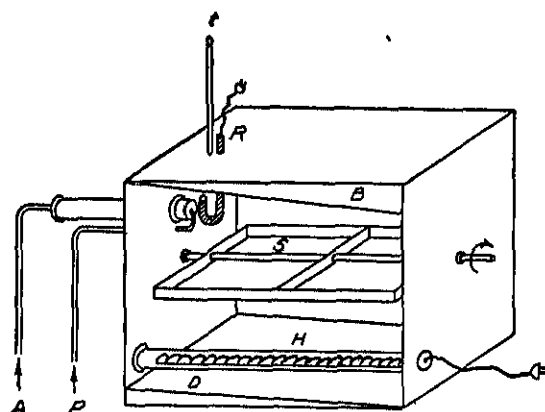



Figure 8. Perspiration-spray cabinet.

The synthetic "perspiration" is prepared according to the following formulation:[26]

*Acid Perspiration Solution*

| *Material* | *Grams* |
|---|---|
| Sodium chloride | 10 |
| Lactic acid, U.S.P. (85%) | 1 |
| Disodium orthophosphate | 1 |
| Water | 988 |

Duplicate or quadruplicate 7 by 7 inch specimens are placed in the cabinet for an 8-hour period, being sprayed intermittently at 1-hour intervals with 30 cc. of the perspiration solution The specimens are finally conditioned for 24 hours in the standard atmosphere and tested for flameproofness using the 45°-Microburner flame test

In the testing of water-soluble flameproofing agents, the spray should be adjusted such that the specimens do not become oversaturated and cause dripping of solution from the fabric Actually, extensive practical wear tests have shown that water-soluble retardants can be effectively leached from the fabric by profuse perspiration.

[26] Federal Standard Stock Catalog—Section IV, Part 5, p. 15. CCC-T-191a. (Apr 23, 1937.)

## 8. Moisture Vapor Permeability

*Robert W. Little*

One of the requirements for flameproofed fabrics intended for u articles of clothing is that the fabric shall allow a free passage of vapor in order that an excessive heat load is not imposed upon the w of the garment. The most reliable method of determining this fabric erty would be to carry out heat load studies and observe the perform of the fabric when in actual use on human subjects. This type of ex ment has been carried out on flameproofed fabrics and is describ Section 10 of this chapter. Since such extensive experiments are gen impractical it is desirable to have a simple laboratory test whicl serve to evaluate the resistance of the fabric to the passage of moi vapor.

A great many different methods have been developed for testin vapor permeability of fabrics, paper, leather and various sheets and The reader is referred to the literature for a detailed picture of the dures[27,28,29,30,31,32] and apparatus[33,34] employed. A bibliographical sum of the available methods has recently been presented by the st The Institute of Paper Chemistry.[35] In general the tests consist method of measuring the rate at which water vapor passes thro sheet from a region of high humidity to one of lower moisture vapo tent. The method of Lyman Fourt and Milton Harris of the Textile F dation[36] relates this passage of water vapor to the intrinsic resista the fabric. The intrinsic resistance, expressed in terms of equivalent timeters of still air, is determined for a fabric before and after th plication of a flame-retardant material, thus determining whether the flameproofing treatment has impaired the passage of water through the cloth.

The majority of the vapor permeability techniques measure the resistance set up by a fabric system. This includes the appreciab sistances of the air layers on each side of the fabric which are ver

[27] Hyden, W. L., *Ind. Eng. Chem.*, 21, No. 5, 405 (1929).
[28] John, R., *Tech. Assoc. Papers*, 20, 90 (1937).
[29] Holwech, W., *Papir J.*, 20, 233 (1932).
[30] Hobbs, R. B., *J. Am. Leather Chem. Assoc.*, 36, 346 (1941)
[31] Herfeld, H., *Collegium*, 65 (1941).
[32] Sears, G. R., Schlagenhauf, H. A., Given, J. C., and Yett, F. R., *Paper Tr* 118, No. 3, 39 (1944).
[33] Noll, A., *Papier-Fabr. Wochbl. Papier fabr.*, No. 5, 151 (1944).
[34] *Modern Packaging*, 16, 78 (1942).
[35] *Paper Trade J.*, 121, No. 16, 33 (Oct. 18, 1945).
[36] Report No. 243, Committee on Aviation Medicine, N.R.C. Div. of Me (Jan. 7, 1944).

pendent upon the conditions of test. By comparing the total resistances of two systems, one of which contains one more layer of fabric than the other, the intrinsic resistance, or the resistance attributable to the fabric alone, may be obtained. This technique of Fourt and Harris was felt to be more applicable to fabrics and is presented here as one of the better methods available.

The apparatus required consists of the parts illustrated in Figure 9 along with a suitable conditioning box or conditioning room in which the

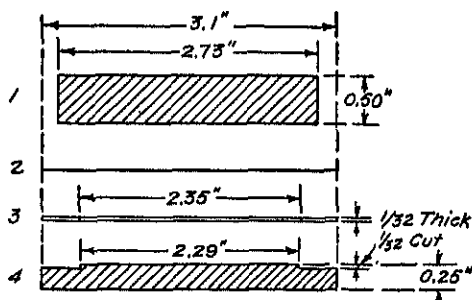
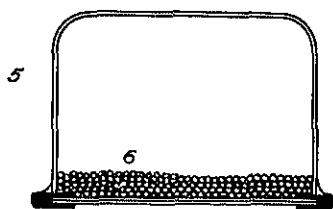



Figure 9. Moisture vapor permeability apparatus.

assemblies may be exposed to an atmosphere of high and constant humidity. As employed in the experimental program of the Columbia University Flameproofing project, the assemblies were placed on a wire screen suspended in the conditioning room. Since the fabric specimens are conditioned in this standard atmosphere of 70° F. and 65% R.H. prior to test, this avoids any pickup of moisture on the part of the fabric in the early stages of the test.

Nine circles of fabric, 3.1 inches in diameter, are cut using one of the aluminum rings as a pattern. These provide specimens for a vapor permeability measurement on 1, 3 and 5 layers of the fabric. The specimens

should be taken from various parts of the cloth sample to minimize e
due to non-homogeneous treatment.

The steel sealing disc and a cup of sealing wax are kept on a hot
throughout the preparation of the assemblies. A satisfactory sealing
may be made of a 50–50 mixture of paraffin and beeswax. An alum
ring is placed on the jig and the outer half of the upper surface pa
with sealing wax. A corresponding circle of wax is painted aroun
edge of one surface of a fabric specimen, the cloth disc placed or
ring with the two waxed surfaces together and the two sealed togeth
placing the hot sealing disc on top of the fabric. For the 1-layer as
bly, this procedure is repeated sealing a second aluminum ring or
other side of the fabric. In the case of the 3- and 5-layer assemblies
adjacent cloth discs are sealed together as described above, placing a
of sealing wax on both discs, pressing them carefully together and se
with the hot steel disc. In each case the last cloth layer is topped wi
aluminum ring. Finally, the edges of the completed assemblies are pa
with wax to assure an airtight seal, and the three assemblies conditi
for 24 hours at 70° F. and 65% R.H. Twenty grams of Drierite are p
in each of three tanning dishes, a fabric assembly placed on each dish
sealed in place with sealing wax. The final assemblies are placed f
side down on a large-mesh wire platform which is in the conditioning r
A uniform current of the moist air passes steadily over the surface o
exposed fabric. The entire assemblies are weighed on an analytical
ance at 30-minute intervals over a period of 2.5 hours. Just after
weighing the desiccant is mixed by gently shaking the dish.

Resistance being the reciprocal of permeability, a convenient uni
expressing the resistance of a fabric has been selected as the length o
equivalent column of still air through which water vapor would di
at the same rate under the same conditions of temperature, pressure
concentration gradient. The total resistance of a system, then, woul
expressable in the following form:

$$R = \frac{1}{Q} D(\Delta C) A t$$

where:

$R$ = total resistance of the system, the resistance to the diffusion of water vap
pressed in equivalent centimeters of ideal still air.
$Q$ = mass of water transferred by diffusion, in grams.
$D$ = diffusion constant in $cm^2/sec$.
$\Delta C$ = difference in concentration of water vapor in $gms/cm^3$.
$A$ = area of fabric through which moisture travels in $cm^2$.
$t$ = time interval, in seconds.

In order to clarify the calculation of test results, a sample calcula
is given in the following section for a measurement of 8.5 oz. herringb
twill in a room at 70° F. (21.1° C.) and 65% R.H.

According to International Critical Tables, the diffusion coefficient, $D$ varies with the absolute temperature, $T$, and the barometric pressure, $P$ (mm. Hg) as expressed in the equation:

$$D = 0.220 \left(\frac{T}{273}\right)^{1.75} \times \frac{760}{P}$$

As an approximation between 0 and 50° C., this may be replaced by:

$$D = 0.22 + 0.00147(\text{m}^\circ \text{ C.})$$

Since the temperature in this case was 70° F. or 21.1° C.:

$$D = 0.22 + 0.00147(21.1) = 0.251 \text{ cm}^2/\text{sec.}$$

The concentration difference, $\Delta C$, in grams/cm³, can be obtained from the relative humidities $H_1$ and $H_2$, the absolute temperatures $T_1$ and $T_2$, and the corresponding saturation vapor pressures $p_1$ and $p_2$ on each side of the fabric as:

$$\Delta C = \frac{MW_{H_2O}}{G.M.V.} \times \frac{273}{760}\left(\frac{p_1 H_1}{T_1} - \frac{p_2 H_2}{T_2}\right)$$

Since, however, the temperature and pressure both inside and outside are the same and the concentration of water vapor on the inside is essentially zero:

$T_1 = T_2 = 273.1 + 21.1 = 294.2°$ K

$p_1 = p_2 =$ saturation vapor pressure at 21.1° C = 18.76 mm.

$H_1 - H_2 =$ difference in relative humidity from one side of the fabric to the other $= 0.65 - 0 = 0.65$

$MW_{H_2O} = 18$

$G.M.V. = 22{,}400$ cc under standard conditions and:

$$\Delta C = \frac{18}{22{,}400} \times \frac{p}{760} \times \frac{273}{T}(H_1 - H_2) = \frac{18}{22{,}400} \times \frac{18.76}{760} \times \frac{273}{294.2} \times 0.65$$
$$= 1.198 \times 10^{-5} \text{ gm/cm}^3$$

Also, since the exposed fabric disc has a diameter of 2.35 inches and the area is to be expressed in cm²:

$$A = \left(\frac{2.35 \times 2.54}{2}\right)^2 \times 3.1416 = 28.00 \text{ cm}^2$$

finally:

$t = 60\,M$, where $M$ = time interval in minutes between successive weighings

Thus substituting in the original equation:

$$R = \frac{M}{Q} \times 0.251 \times 1.198 \times 10^{-5} \times 28 \times 60$$

or:

$$R = 5.05 \times 10^{-3} \frac{M}{Q}$$

$Q$ is obtained by differences in successive weighings and along wi
time elapsed in minutes is then used in the above equation to cal
the total resistance $R$.

The data for the sample calculation are as follows:

| No. of Layers of Cloth | Time | Wt. of Assembly, gms. | $Q$ | $M$ | |
|---|---|---|---|---|---|
| 1 | 2 : 08 P.M. | 69.3069 | —— | — | |
| 1 | 2 : 40 P.M. | 69.4432 | 0.1363 | 32 | |
| 1 | 3 : 10 P.M. | 69.5853 | 0.1421 | 30 | |
| 1 | 3 : 40 P.M. | 69.7115 | 0.1262 | 30 | |
| 1 | 4 : 12 P.M. | 69.8218 | 0.1103 | 32 | |
| | | | | | A |
| 3 | 2 : 27 P.M. | 70.1872 | —— | — | |
| 3 | 2 : 57 P.M. | 70.2843 | 0.0971 | 30 | |
| 3 | 3 : 27 P.M. | —— | —— | — | |
| 3 | 3 : 57 P.M. | 70.4977 | 0.2134 | 60 | |
| 3 | 4 : 27 P.M. | 70.5073 | 0.0096 | 30 | |
| | | | | | A |
| 5 | 2 : 19 P.M. | 83.1336 | —— | — | |
| 5 | 2 : 47 P.M. | 83.2082 | 0.0746 | 28 | |
| 5 | 3 : 17 P.M. | 83.2969 | 0.0887 | 30 | |
| 5 | 3 : 47 P.M. | 83.3789 | 0.0820 | 30 | |
| 5 | 4 : 17 P.M. | 83.4694 | 0.0905 | 30 | |
| | | | | | A |

The intrinsic resistance of one layer of fabric is obtained as fo

$$R_1 \text{ layer} = \frac{R_3 \text{ layers} - R_1 \text{ layer}}{2} = \frac{R_5 \text{ layers} - R_3 \text{ layers}}{2}$$

also:

$$R_1 \text{ layer} = \frac{R_5 \text{ layers} - R_1 \text{ layer}}{4}$$

By these subtractions we cancel out the effect of the surface lay
air on both sides of the cloth as well as the effect of the Drierite
side.

Using the sample data:

$$R_1 = \frac{1.50 - 1.24}{2} = \frac{0.26}{2} = 0.130 \text{ cm.}$$

$$R_1 = \frac{1.75 - 1.50}{2} = \frac{0.25}{2} = 0.125 \text{ cm.}$$

$$R_1 = \frac{1.75 - 1.24}{4} = \frac{0.51}{4} = 0.127 \text{ cm.}$$

Therefore, the intrinsic resistance of 8.5 oz. herringbone twill is
cm. The precision of the measurement is approximately ± 0.0
although this factor will depend greatly upon the allowed variation
relative humidity.

## 9. Surveillance and Tendering Tests

*Henry A. Rutherford and Robert W. Little*

The application of a finish or a coating to a cotton textile frequently raises the question of whether the treatment has an adverse effect on the useful life of the material. Thus, many laboratory methods of ascertaining the stability of a fabric toward light, heat, moisture, mildew, etc., have been devised. These accelerated methods are desirable because of the impracticality of drawn-out and laborious service testing, but unfortunately they are often a completely inadequate substitute.

The conditions used in any of the so-called tendering tests are necessarily arbitrary, but are designed to bring into play those factors which are expected to contribute to the deterioration of the material during use. For example, the stability of a fabric during normal storage conditions might be ascertained by its behavior at some elevated temperature. Materials whose normal use constitutes exposure to the elements must be tested by a more complicated means involving the use of heat, light, and moisture. The reliability of the evaluation procedures is of utmost importance, and it may be said that the more drastic the conditions of accelerated testing, the greater the possibility of arriving at a false evaluation of the durability of a fabric during normal use.

The lack of standard test procedures emphasizes the difficulties involved in this type of work. A survey of the literature, which for the most part consists of government specifications, reveals a number of surveillance and tendering tests. Changes in details of procedure have been made from time to time, but in every case the general form of subjecting fabrics to heat, light and/or moisture separately or together has been followed A description of accepted (but not necessarily proved) procedures in force in May, 1945, which might possibly apply to fire-resistant fabrics, is presented.

U. S. Army Specification No. 100–48, dated May 11, 1945, pages 35 and 36, lists the following: [87]

"4. Accelerated aging tests.—

"4a *Oxygen bomb test.*—The given specimen of coated fabric shall be exposed to an atmosphere of oxygen at a pressure of 300 pounds per square inch and a temperature of 158° F. (70° C.) for a specified period of time. After exposure, the coating on the fabric shall show no signs of becoming stiff and brittle, nor soft and tacky, nor shall the loss in tensile

[87] Other references to tendering tests are as follows· Yearbook of the American Association of Textile Chemists and Colorists, A.S.T.M. Standards on Textile Materials; Federal Specification CCC–D–746; Q.M.C Tentative Specification JQD 242; and U. S. Army Specification 6–345. These specifications are not necessarily in force.

strength, as determined by the grab method, exceed a specified per
of the original tensile strength.

"4b. *Aging test, 100° C., 48 hours.*—The treated material sha
stored in an oven at a temperature of 100° C. for 48 hours and th
sulting pH determined in the specified manner.

"4c. *Aging test, 175° F., 5 days.*—The sample of the treated ma
shall be placed loosely inside a quart Mason jar. The open jar conta
the specimen shall be exposed to standard atmospheric condition
24 hours. At the end of the 24-hour period the quart jar shall be cl
airtight, and then subjected to a temperature of 175° ± 5° F. for 5
The breaking strength of the material shall then be determined.

"5. Resistance to accelerated weathering.—

"5a. *Test specimen.*—A sample of specified dimensions, with the
dimension in the direction of the filling shall be clamped to the i
rotating rack of the accelerated weathering test machine and expos
the conditions described below.

"5b. *Accelerated weathering test machines.*—One of the following
commercial machines as specified shall be used.

"5b (1). *Accelerated weathering machine.*—Atlas Electric Device
Model DL-TS. This double carbon arc apparatus shall be operated
ambient temperature as specified, and in accordance with the direc
furnished by the manufacturer. The light and water spray shall b
justed to provide light continuously and water intermittently in a
stant cycle of 17 minutes without water and 3 minutes with water
water shall be discharged at the rate of 0.5 gallon per minute an
drum shall rotate at the rate of 1 revolution per minute.

"5b (2). *Accelerated weathering unit.*—The apparatus shall cons
a vertical carbon arc mounted at the center of a vertical cylinder
arc is designed to accommodate two pairs of carbons, No. 22, uppe
bons, and No. 13, lower carbons; however, the arc burns between
one pair of carbons at a time. The arc shall be surrounded by pan
Corex D glass or other enclosure having equivalent absorbing or t
mitting properties. The glass shall be cleaned at least once every 24
of operating time. The arc shall be operated on 60 amperes and 50
across the arc for alternating current of 50 amperes and 60 volts acro
arc for direct current. The specimens for test shall be mounted on a
ing rack inside the cylinder and facing the arc. The diameter of the
ing rack shall be such that the distance from the center of the arc
face of the specimen is 18¾ inches. The rack shall rotate about tl
at a uniform speed of about 1 revolution in 2 hours. Spray nozzles
be mounted in the tank so that the specimens shall be exposed to w
once during each revolution of the rack. An X-1A National Carbo
weathering unit burning National Sunshine cored and copper-coate
bons will fulfill the above.

"5b (3). *Single arc accelerated weathering machine.*—The apparatus shall consist of a vertical carbon arc mounted at the center of a vertical metal cylinder. The arc shall be enclosed in a clear globe of No. 9200 PX Pyrex glass 0.0625 inch thick or other inclosure having equivalent absorbing and transmitting properties. The globe shall be cleaned when the carbons are changed or at least once every 36 hours of operating time. The arc shall be operated on 13-ampere direct or 17-ampere 60-cycle alternating current with the voltage of the arc 140 volts. The specimens for test shall be mounted on the inside of the cylinder facing the arc. The diameter of the cylinder shall be such that the distance of the face of the specimens from the center of the arc is 14¾ inches. The cylinder shall rotate about the arc at a uniform speed of approximately three revolutions per hour. A water spray shall strike each 2-inch-wide specimen in turn for about 1 minute during each revolution of the cylinder. An Atlas Electric Devices Co. single-arc weather-o-meter will fulfill the above conditions."

It must be emphasized again that these tests do not necessarily *predict* the behavior of flameproof fabrics during actual use, and that their primary function is to serve as a means of detecting materials or coatings which, under certain conditions, might have adverse effects on the fabric. They are also useful in ascertaining the effects of one treatment relative to another. For example, it has been observed that cotton duck, treated so as to be fire, water, weather, and mildew resistant, which contains an unstable chlorinated paraffin, exhibits an increase in acidity (decreased pH) during heating at 100° C., whereas one which contains a stable type material shows no change in this respect. Increase in acidity may be regarded as undesirable because of the sensitivity of cellulose to acids.

In most instances, the resistance of the fabric to aging is determined by loss in strength, but it is difficult to establish satisfactory levels of performance. Other tests, such as tearing strength and fluidity, are sometimes useful. The latter is of value in detecting certain types of incipient damage in cellulose which is not always revealed in losses in strength (see oxidation of cellulose). As a general rule, flameproof fabrics are also required to maintain their initial properties of flameproofness during exposure under the conditions of the various tendering tests.

At the outbreak of World War II, considerable impetus was given to the problem of evaluation of textiles by tendering tests. One of the most important items for consideration was duck, cotton; fire, water, weather and mildew resistant, because of its wide use in tentage and tarpaulins. The results of three years' work [38] showed that it was impossible to evaluate the potential life of fabrics of this type by any one of a number of accelerated laboratory tests. This is because the performance during natural weathering is largely dependent upon the location of exposure. In other words, no precise and fixed behavior of a fabric could be estab-

[38] Sponsored by the Office of the Quartermaster General

lished. Thus, it was made clear that the potential serviceability of f
for tentage can be reliably judged only by subjecting them to ex
exposure, and that the service life will depend upon the condition
vailing at the point of usage.

Evaluation of duck, cotton; fire, water, weather, and mildew res
under U. S. Army Specification 6–345 is based primarily on perfor
during exterior weathering in Yuma, Arizona, and New Orleans, Lou
for a period of six months, April through September being preferred.
locations were chosen on the basis of their wide divergence in climati
ditions. The results of exposures made in desert areas lack the com
tion introduced by the action of microorganisms. Exposures in
tropical or tropical areas have the primary function of establishi
resistance of fabrics to mildew in the presence of sunlight and ra
and ordinarily do not subject fabrics to the stringent conditions o
light intensity at low moisture levels.

In the course of the experimental work carried out under ]
Project Q.M.C. #27 at Columbia University several surveillance an
dering tests were employed in order to anticipate the relative beha
variously flameproofed fabrics in the course of normal service. Co
tive data were desired after long-term exposure under normal a
conditions and also following short exposures to the extremes of te
ture and humidity. As mentioned above, it was highly desirable th
accelerated conditions should not be so severe as to cause chem
physical changes in the flameproofing agent which would not als
in time under the conditions of actual usage. The four test con
selected, which will be briefly discussed in the following pages
(1) prolonged indoor storage under existing conditions, (2) extend
door exposure under prevailing weather conditions, (3) accelerat
storage for 2, 3 and 4 weeks at 150° F., and (4) accelerated
storage for 2 weeks at 120° F. and 85% R.H.

**Indoor Storage.** Due to several experiences with the loss of eff
ness of certain water-soluble retardants on prolonged indoor stora
surveillance procedure was adopted for a study of the temporary
proofing agents. The testing procedure consists simply of sus
treated fabric samples in a closed room for long periods of time, re
test specimens at weekly or monthly intervals and testing for flam
ness or fabric strength after conditioning for at least 24 hours
standard atmosphere. Care should be taken that there are no f
creases in the stored samples since it has been found that contact b
fabric surfaces interferes with the vaporization or sublimation of
constituents. Since in a surveillance test of this type the existing
tions are extremely variable, it is well to conduct all experimen
comparative basis referring to a standard fabric which is subjecte
same test period. The temperatures and humidities encounter

naturally vary greatly from one part of the country to another. The tests at Columbia were performed during the summer and fall months, the temperature ranging from 65 to 95° F. under nearly all possible values of relative humidity.

**Outdoor Exposure.** In a study of durable flameproofing treatments it is desirable to know the effect of outdoor weathering upon the permanence of the flameproofness and the properties of fabric strength. The procedure consists of stretching large samples of treated fabric on a metal frame and placing the frame in such a manner that the samples are completely exposed to wind, rain and sunlight. The supporting frames in this instance were supported at an angle of 45° facing the southeast, and the samples exposed to typical East Coast fall weather. In this case also it is essential that all data which are to be subsequently compared be collected in parallel tests under the same existing conditions. If this is not possible, the use of a standard reference fabric will permit some qualitative comparisons.

**Accelerated Dry Storage.** Flameproofed fabrics employed in articles of military clothing might well be exposed to long periods of storage prior to issue for use. It is imperative that during the storage period the garment does not undergo any serious impairment of its strength or flameproof characteristics. In an attempt to simulate the severe dry storage conditions which might be encountered in arid regions, a tendering test was employed wherein fabrics were exposed to a temperature of 150° F. for 2-, 3- and 4-week periods.

The tendering chamber consists of a large, triple wall, forced circulation oven in which the temperature can be controlled to ± 1° F.

Samples of the treated fabric are suspended in the oven vertically, specimens being withdrawn at the end of 2, 3 and 4 weeks. In each case the specimens are reconditioned for at least 24 hours at 70° F. and 65% R.H., reweighed to determine possible loss in add-on and subjected to the tensile or flameproofness test.

**Accelerated Humid Storage.** In an attempt to simulate humid storage under severe tropical and jungle conditions tendering tests were also carried out for a period of 2 weeks at 120° F. and 85% R.H.

The tendering cabinet in this case was specially constructed for the purpose and is shown in Figure 10. The 4-inch walls contain 2 inches of rock-wool insulation and the doors are sealed by padding with a layer of felt around the jambs. Heating is accomplished by means of a nichrome electric grid heater regulated by means of a gas-mercury thermostat and suitable temperature regulator relay. The cabinet temperature can be maintained to ± 0.5° F. The humidification system consists of a large cheesecloth screen continually wetted by a stream of hot running water. The air in the cabinet is circulated through the wet screen by means of a small electric fan. The relative humidity is constant to ± 3%.

The test procedure employed is essentially as described for th
erated dry storage test.

As has been previously pointed out these accelerated tenderir
are valuable in the study of flameproofed fabrics in spite of the fa

A. Side View
Showing thermostat, dry bulb, fan and heating grid.

B. End View
Showing wet bulb, cheesecl over hot water spray and

Figure 10. Humid tendering cabinet.

they may not exactly predict the performance of the fabric under
conditions of usage. They serve particularly well in comparing t
formances of several differently treated materials, as is often desi
development work and furthermore are of great value as screeni
cedures. The ability to closely duplicate the conditions allows co

between experiments which may have been conducted over a very wide interval of time. This is a definite advantage over long-term exposure tests under existing weather conditions where all data which are to be considered comparatively must be obtained concurrently. The interpretation of results of either laboratory or field tests is unfortunately not a routine matter, and the limits or tolerances allowed in the various procedures described herein cannot be fixed. These limits are usually based upon personal judgment and experience, taking into account the conditions of the test.

## 10. Physiological Heat Load Experiments

*William R. Christensen*

Experiences of the past few years have clearly demonstrated that physiological heat load must be considered in the selection of uniforms for military personnel operating in tropical or desert terrain. It is essential that those uniforms which seriously interfere with the dissipation of bodily heat be avoided under such circumstances. If such garments are issued, they are likely to be discarded as soon as the heat becomes excessive (and their protective qualities thereby effectively eliminated) or, if retained, the incidence of heat exhaustion may be increased. An evaluation of the physiological heat load of military garments is, therefore, advisable or even essential.

Accurate accomplishment of this task requires considerable care and time. Very special types of equipment and a large number of trained, cooperative subjects are necessary. However, its value is manifest. In this section an attempt is made to present a simple but adequate test technique. The method described is based largely on the experiences of the Climatic Research Laboratory. This presentation is in no way intended to be comprehensive.

Fundamentally, all approaches to this problem are based on consideration of the human body as a heat-producing machine. The importance of imposed physiological heat load stems from the fact that the body temperature must be regulated within very close limits if operating efficiency is to be maintained. When exposed to low ambient temperatures, the human maintains a satisfactory mean temperature by certain physiological adjustments and through the addition of clothing, the thermal insulation of which reduces the loss of heat. At high ambient temperatures, the body must lose more heat or its temperature will mount and physiological breakdown will eventually occur. This heat is principally dissipated through radiation, conduction, convection, and evaporation. In any given case, the relative magnitude of the loss through each of these avenues is determined solely by the existing ambient conditions, *i.e.*, dry bulb temperature, intensity of solar and terrestrial radiation, air movement and

wet bulb temperature. Obviously, the most immediate effect of an ex
sive load upon the cooling mechanisms of the body would be a rise in
average temperature of the tissue mass. This is reflected by an increas
the skin and rectal temperatures. Concomitantly the cardiac output is
creased, the most obvious sign being an increase in pulse rate,
peripheral vasodilation occurs. Sensible perspiration appears and incre
roughly in proportion to the elevation of skin temperature. The majo
of these responses can be interpreted as attempts to increase amoun
heat loss. Their relative efficiency differs widely according to the c
conditions of wet and dry bulb temperature, radiation, and air movem
However, it is quite apparent that clothing of any type would act as
terrent to the efficient dissipation of heat. The thermal insulation it
vides reduces conductive losses when the ambient temperature is b
that of the body surface. Convective cooling currents are largely el
nated because free circulation of air is prevented by the clothing. Garm
also provide a radiation barrier. And, because they present a barrier to
diffusion of water vapor, evaporative heat loss is reduced. Under 1
circumstances of high temperature and humidity, therefore, clothing
be considered to constitute a barrier to heat dissipation by the body
outlined above, the physiological effects which may be expected ar
increase in rectal temperature, skin temperature, blood volume, car
output, pulse rate, peripheral blood flow, oxygen consumption and s
production. If such trends are allowed to continue, efficiency is soor
duced and irreversible changes may ensue. Obviously the immediate s
tion is to discard all clothing. Many peoples living under conditions im
ing heavy heat loads have come to this solution. However, the unac
tomed soldier from temperate areas requires the protection against s
radiation, insects, skin trauma, etc., which a garment provides. Like
if there are no garments there can be little or no protection against fl

It is entirely logical to assume that the magnitude of the response
heat would be directly related to the magnitude of the heat load impo
This has been proved experimentally for a majority of these values. Th
fore, by exposing human subjects in various garments to controlled co
tions, an evaluation of the heat load imposed by the garments ma
obtained from the magnitude of the physiological changes which the
duce. Some of the physiological changes, however, can be more rea
adapted to testing techniques than others. Determination of blood
and oxygen consumption is too difficult for routine use. Changes in b
volume probably do not appear rapidly enough. Because of this, mos
vestigators have depended upon measurement of skin temperature, r
temperature, pulse rate, and sweat production for evaluation of garm
The measurement of rectal temperature, pulse rate and sweat produ
is relatively easy, but accurate determination of skin temperature
quires the use of radiometers. These instruments are difficult to use

require constant, careful calibration. Because of this, skin temperatures are also often discarded. This omission leaves sweat loss, rectal temperature and pulse rate as the chief criteria. The response of the sweat rate to any given change in conditions is by far the greatest. Therefore, this is probably the most sensitive and accurate of these determinations.

Having thus established physiological criteria for evaluation of imposed heat load, it is important to consider the equipment and subjects. The success or failure of such experiments will depend largely upon the chamber used and the subjects selected. Rigid control of ambient conditions within the experimental chamber is essential. Since the over-all heat loss from the body is determined by the combination of wet and dry bulb temperature, radiation, and air movement, it is quite apparent that all of these factors must be very carefully controlled. Small variations in wet or dry bulb temperature, wall temperature or wind velocity under severe environmental conditions will oftentimes produce more marked physiological changes than the garments themselves. The chamber should be such that it will maintain wet and dry bulb temperatures within ± 1.0° F. It is essential that this control be maintained throughout the daily experimental period as well as from day to day. Wall temperatures, including ceiling and floor, must be similarly controllable so that the radiation factor is constant. Wind velocity should not vary more than ± 0.1 mile per hour. The miscellaneous equipment required includes a treadmill, providing very constant and reproducible walking speeds, a balance of sufficient sensitivity to weigh the subjects to within ± 5 grams, rectal thermometers and cardiotachometer or stethoscope. The cardiotachometer is preferable for recording pulse rate since it supplies a permanent record and is not subject to the errors of personal interpretation With this equipment, there has been constituted a rigidly controlled environment in which work of a prescribed, reproducible rate may be performed which is equipped with instruments enabling the measurement of the expected physiological changes.

What of the experimental subjects? As far as can be determined, men of any bodily size or configuration are suitable However, it has been generally found that individuals of the pyknic type are rather unsatisfactory in that high temperature exposures are more difficult for them and their results are not as reproducible as others. Under any circumstances those selected should be physically vigorous and willing to undergo arduous exposures to high temperatures over extended periods of time. It is also essential that they realize that fairly regular eating and sleeping habits must be maintained and that excessive indulgence in alcohol be strictly avoided throughout the period of the test. After their selection, all subjects must be physically trained and acclimatized. Both training and acclimatization affect the subjects' physiological responses to any given set of conditions. A trained man completes a prescribed period of walking

on the treadmill with lower pulse rate, rectal temperature, skin temp
ture, and less weight loss. The same is true in the case of acclimatiza
Obviously, therefore, untrained and unacclimatized subjects would n
in a basal state and could not be expected to achieve reliable or re
ducible values from day to day until they had been so conditioned. T
results would be worthless. Training and acclimatization should be ca
out under conditions which duplicate those outlined for the test rou
Both can be accomplished simultaneously. Five days of exposure to
exercise and ambient conditions to be used in the test procedure
suffice. The major portion of acclimatization is known to be comp
within this period of time and, if the subjects are in reasonably good
dition initially, no further training will be required.

Before setting up the exact routine to be used in evaluating the
ments, it is essential that the criteria for differentiating them be es
lished. The physiological data, as outlined, will include pulse rate, r
temperature, sweat loss, and possibly skin temperature. In the first pla
must be realized that there is no absolute standard with which these va
may be correlated. The physiological responses of different individua
the same heat stress are extremely variable and pulse, sweat rate
rectal temperature bear no simple relationship to the working ability o
likelihood of failure in an individual. Therefore, all evaluations n
necessarily be comparative, *i.e.*, responses of the same subject mus
compared. It would be extremely difficult to perform a physiological
periment of the type required with a sufficient number of subjects to
out inter-individual differences. The performance of a subject in
garment must be compared with his performance in another This ca
done accurately as long as experimental conditions are as carefully
trolled as outlined. What, however, should be used as the ultimate st
ard of comparison? Some of the criteria which might be considered a
follows: (a) the absolute limits of temperature and humidity the su
can stand while wearing the test uniforms, (b) the extent of the phy
logical changes induced by standard work periods in the garments b
studied, or (c) the amount of work required to induce specified phy
logical responses in subjects wearing these uniforms. Any one of t
methods may be used. In some instances a knowledge of the upper li
of temperature or work which can be tolerated by a group in a unif
will be of value. However, the comparison of the physiological char
induced by standard work periods is the easiest and simplest appro
Naturally a standard garment will have to be selected as the basi
comparison. If a new uniform is being considered, the one it is intende
replace may be used as a standard of comparison.

Comparative experiments of this type require special consideration
order to insure proper control. In addition no conclusions should be dr
unless they can be supported by statistical analysis of the data. Cer

arbitrary limits over and above statistical significance may be established. Either type of consideration requires that the reactions of individuals be compared only among themselves, *i.e.*, that there be no inter-individual comparisons. This means that all subjects in a test group must wear all of the test items. Thereby an individual's reaction in one outfit can be compared with that in another outfit. Likewise, it is essential that experimental items be rotated among subjects according to a Latin Square technique and that, in any single phase of the work, all items undergoing comparison be represented. If only two subjects can walk on the treadmill simultaneously, only two uniforms can be compared. On the first experimental day each subject wears one of the two uniforms; on the second day the types are exchanged. Thus a máximum of control is obtained. For adequate statistical consideration of such paired data a sampling of at least six and preferably eight or ten subjects is required. In accordance with the material outlined above the data considered will include weight loss during the period of exercise, the rectal temperature, pulse rate and skin temperature at the completion of the period of exercise.

Thus far nothing has been said concerning such details as length of exercise period, severity of exercise and ambient conditions to be used. No categorical statements can be made. Some investigators have employed 4-hour periods, thus insuring that equilibrium between heat production and loss will have been attained. Others have used only 1-hour periods, since differences in garments will have appeared by this time even though equilibrium may not have been reached in some instances. Experience at the Climatic Research Laboratory has shown this to be a suitable method. Under any circumstances all experimental subjects should undergo a definite pre-exercise rest period in the chamber. Only by this means can a fairly standard state in all subjects be assured for the beginning of the testing period. The severity of the exercise may vary considerably. However, an attempt should be made to duplicate the field conditions expected Great care must be taken to adjust the exercise to the ambient conditions in order to avoid imposition of too great a burden upon the subjects. The ambient conditions under which testing has been carried out have varied considerably. Obviously it is desirable that the garments be investigated under conditions of temperature, humidity, radiation and air movement similar to those under which they are to be used. Significant differences are more likely to be revealed when certain ambient conditions are used. However, if the garment is never used under such circumstances the difference is meaningless.

Strictly speaking, the subjective appraisal of test items has no place in a discussion of techniques of evaluating heat load. However, there are certain features of garments which are exposed remarkably clearly by wear under simulated tropical or desert conditions, namely, drag (the tendency of garments to restrict motion by adhering to the skin), skin

sensation and subjective coolness. They are equally as importar posed heat load in determining whether or not a uniform will b accepted. Because of this it is probably desirable, in all garment sons, to obtain an interview at the completion of the comparison all subjects are asked to rate the garments in the order of their pi in regard to (1) coolness, (2) drag, (3) skin sensation, and (4) preference. The data obtained may be analyzed statistically.

Through correlation of physiological and subjective data, coll outlined above, one may form a reasonable conclusion as to the acceptability of any uniform for wear under tropical or desert co

## 11. WEAR TESTS

*E. Folger Taylor*

A specially designed garment, or a garment of standard design special fabrics or treated fabrics, must be proved for wearing ab fore it can be adopted for general use by the Army. Wear tests of types are commonly used. Accelerated wear tests, in which the g are continuously subjected to severe wear conditions simulating t countered in combat, are used to evaluate the performance of garments in terms of a standard garment. Normal wear tests, durin the garments are worn in the usual routine of training, maneu garrison work, compare the performance with that of the standard under the same conditions. Special wear tests, in which a group wear the garments under carefully controlled conditions, evalua particular property of the garment. Such tests may take advan natural or artificial environments depending on what property garment is being studied.

Accelerated wear tests are made by the Quartermaster Board a Lee, Virginia, on a combat course designed to expedite tests of design, construction and materials under simulated rigorous fie ditions.

The combat course is illustrated in Figures 11 through 16 and of 22 obstacles, each representing a definite tactical problem and a that might be encountered in most theaters of operation.[80] The c 1700 feet long and each obstacle was selected after an exhaustiv had been made of clothing failures in the field. Thousands of ga that had been salvaged in the theater of operations and the cont United States were carefully analyzed; combat motion picture studied; enlisted and commissioned personnel just returned from areas were questioned; and expert clothing technicians were con As a result the simulated tactical problem which was set up was

[80] Figures and details of description furnished by the Quartermaster Board Lee, Va.

troops approaching and attacking an enemy village and then continuin, on to wipe out an enemy strong point.

The test subjects traverse the course by rushing, crawling, creeping climbing, sliding and jumping. From their first vantage point at the start of the course the soldiers run and take cover behind several natural objects as they approach a railroad embankment, where they climb a revetment, squirm across the heavy coarse slag of the railbed on their stomachs and slide head first down a 30° slide of Belgian Block about 20 feet long. At the bottom they scramble to their feet, run and drop behind a split rail fence. Then the fence is climbed quickly and the soldiers run

*Courtesy of Quartermaster Board, Camp Lee, Virginia.*

Figure 11 Wear test combat course: Descending 20-foot Belgian Block slide

to take cover behind a stone wall. After crossing the wall they run forward taking momentary cover behind trees and logs until a slit trench is reached Here the test subjects rest and then climb over a tree block and advance to a crushed stone road which must be traversed on the stomach. A series of trenches, a road block and finally a cement culvert are traversed before the enemy village is reached.

The village consists of three bombed out houses. The soldiers enter through the window of the first house, make their way under fallen beams, over passages strewn with cement and rubble, up and down wrecked stairways. They traverse two such dwellings in succession and finally cross from the second dwelling to a ruined warehouse by means of a fallen beam. Here the test subjects are confronted by a maze of narrow twisting

*Courtesy of Quartermaster Board, Camp Lee,*

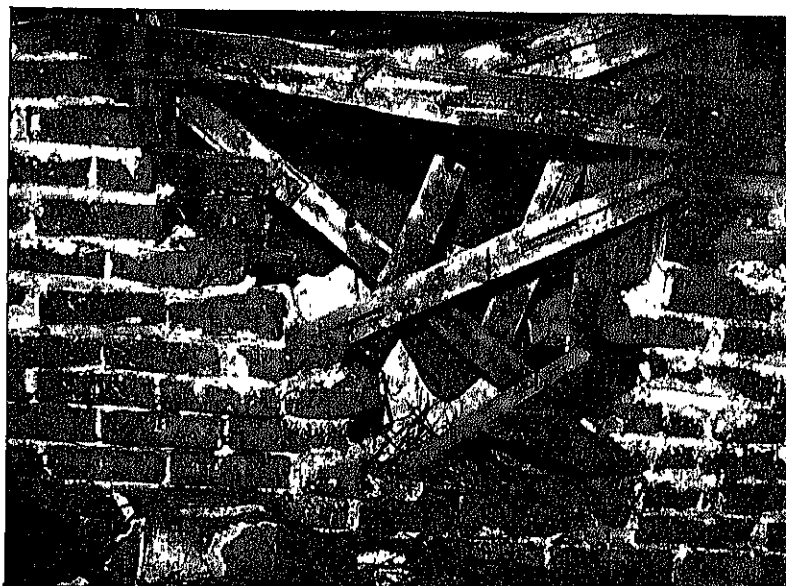
Figure 12. Wear test combat course: Crossing stream on fallen timbe

*Courtesy of Quartermaster Board, Camp Lee, V*

Figure 13. Wear test combat course: Crawling through rubble of bombed-out

*Courtesy of Quartermaster Board, Camp Lee, Virginia.*

gure 14. Wear test combat course: Crossing from ruined house to warehouse on fallen beam.

*Courtesy of Quartermaster Board, Camp Lee, Virginia.*

Figure 15. Wear test combat course: Climbing slag railroad embankment.

passageways between jumbled packing cases and, as the soldiers work
way through them, every inch of clothing is subjected to strain
abrasive action. Following the village is another railroad embankı
which must be climbed and crossed by crawling, after which the sol
creep and crawl through a logged communication trench and net
of forward trenches. As the final objective, the enemy strong point is
proached, the soldiers squirm on their backs under a wire entanglem
roll over a road block and slide down a cement lined tank trap, compl
the traversal of the combat course.

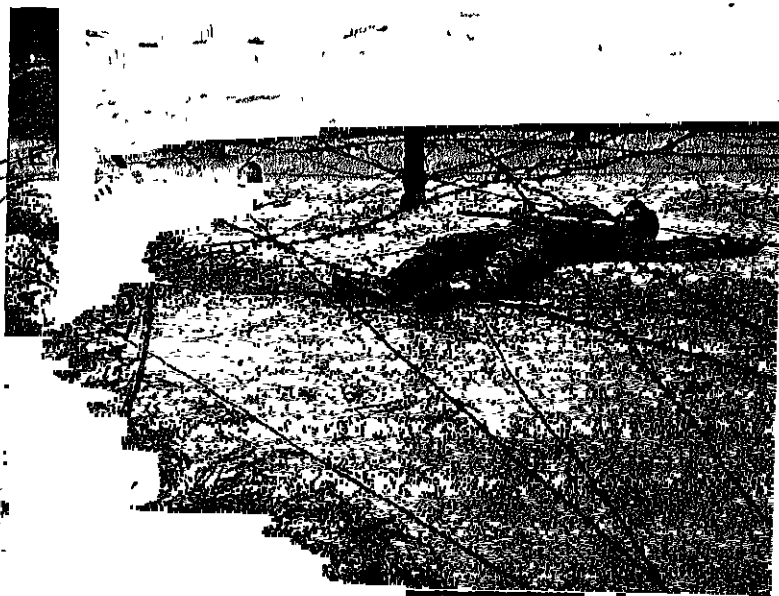



Figure 16. Wear test combat course: Squirming under wire entanglement

To evaluate clothing by means of this course a group of men outfi
with properly fitting garments are sent over the course as many tim
are needed to make the garment unserviceable. The use of correctly fi
garments is of the utmost importance if valid test results and conclu
are to be obtained. After each traverse of the course, the nature, loca
and extent of deterioration or failure are observed. Traverses of the co
are made by the group using control garments as well as the experim
garments and an analysis and comparison is made of the extent and
of deterioration and failures. Since it is possible for a man to traverse
course several times a day and since the best garments rarely stan
many as twenty-five traverses before becoming unserviceable, this co
will yield, in a matter of days, information which would take montl
obtain from field tests.

Normal wear tests consist of a systematic observation of the manner i which various garments perform under whatever conditions of practica use are desired. For instance, a group of subjects may be equipped wit test and control garments and permitted to go about their normal duties Weekly observation of how the garments are wearing can then be made either before or after laundering, or both, throughout the life of the garment. For the best comparison, it is preferable to select groups of test subjects whose normal duties are the same so that the wear may be related, if possible, to the duty. In this way performance of the new garments under conditions of garrison duty, training, maneuvers, can be studied and correlated with the performance of the standard items.

Details of such tests depend upon what performance characteristics the observers wish to study. For instance, in one wear test of flameproofed clothing the object was to determine the wear life of the garment and the flameproof finish when the garments were worn eight hours a day doing routine duties at an Army laboratory. The garments were laundered once a week using the Army mobile laundry equipment and the standard washing procedure. Each week garments were dropped from the test at random and specimens were selected from worn portions of the garments as indicated in Figure 17. Some of these specimens were taken before laundering, the remnants of the garments were then laundered and a second set of specimens taken.

These specimens were tested for tensile strength by the raveled strip method as a means of determining the deterioration of the fabric and for flameproofing by both the 45°-Microburner and the Vertical-Bunsen burner tests to ascertain the extent to which the flameproof finish had failed. The selection of specimens before and after laundering permits a differentiation of the deterioration caused by wear and that caused by laundering. In addition to the deterioration of objective qualities such as tensile strength and flame resistance, a subjective evaluation of the garments can be made on the basis of comments that test subjects have to make about the garments. Tests as outlined above should, of course, be conducted to give data which can be evaluated statistically so that confidence may be placed on the validity of the test results.

Special wear tests can also be designed to evaluate some particular aspect of clothing, or clothing treatments. In the case of flameproof clothing, for military use, it is important to evaluate the action of sweat, rain and sea water on various flameproof finishes. The effect of sweat on the flameproof garments can readily be evaluated in conjunction with the physiological heat load tests. Ordinarily, test subjects do work on a treadmill at a standard rate under conditions of high temperature and high humidity as indicated in the preceding section. The total time of exposure is predetermined and is generally accomplished as the result of a series of work periods. The amount of sweat absorbed by the garments is measured

by weighing before and after use. The action of sweat on the tens strength and flameproofing is measured on appropriate specimens. Si the action of sweat may be spotty because of the manner in which ga ments come in contact with the body, specimens should be chosen fr various parts of the garment to detect such a difference if it occurs. Figu

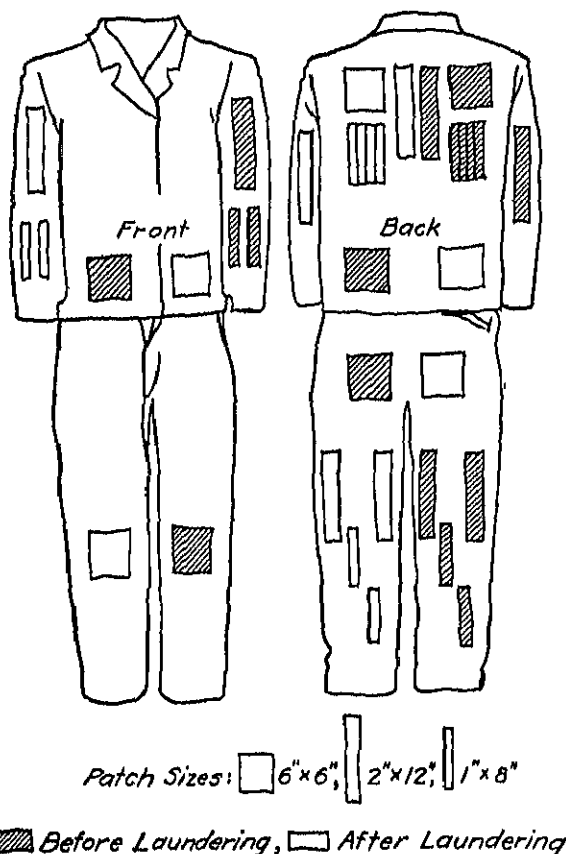



Figure 17. Sampling of worn garments for flame test and tensile test specimens.

17 also represents a suitable method of selecting specimens for t purpose.

The effect of rain is conveniently studied in a so-called "rain cour The rain court is a large room or outdoor space which is equipped witl shower system so designed that the falling water approaches natural r in drop size and terminal velocity. The rainfall can be adjusted from to 3 inches per hour and by operation of auxiliary fan equipment, wi can be superimposed on the rainfall to give the driving effects of a sev storm. In order to maintain the comfort of the test subjects during

exposure, the test garments are worn over other clothing consisting of underwear, socks, shoe pacs, wet-weather parkas and trousers. Periods of exposure can be set for the convenience of the test subjects and continued exposure can be adjusted to whatever total time is desired or samples can be withdrawn at periodic intervals and tested for tensile strength and flame resistance. In general the type and amount of rainfall exposure to be given a treatment can be decided on the basis of preliminary leaching tests. Easily leachable finishes will need only mild rain treatment for evaluation. Thus in the case of a water-soluble salt type treatment where the objective is to determine the minimum amount of rainfall which will remove the flameproof protection, light rainfall of about 0.1 inch per hour and short exposures must be used. But where a finish does not deteriorate under leaching it is sufficient to show that a specific number of hours of heavy rain, *e.g.*, 3 inches per hour, do not affect the garment or flameproof treatment.

Sea water immersion tests are necessary because it has been found that durable treatments of the urea-phosphate type and possibly other new types which may be developed from time to time are reduced in flameproofing efficiency after prolonged contact with water containing appreciable amounts of calcium and magnesium ions. Sea water immersions are designed to simulate operational landings. Where troops are disembarked from landing craft on to the beaches in sea water which varies in depth, some or all portions of the body may be wet for various periods of time. While landing maneuvers could be used for such a test, superior information can be obtained by a controlled immersion test in which the landing operation is simulated in reverse. An appropriate beach is selected where the test subjects wade in water up to the knees for a period of time, then up to the waist for additional time, and finally up to the neck. Samples of these garments are selected for tensile strength and flameproof evaluation in such a manner as to differentiate between the different times of exposure to the action of sea water. Details of the test can be arranged to test any effect or series of effects of sea water immersion, as for instance the effect of a series of alternate immersions and launderings.

Wherever susceptibility to detrimental ion-exchange reactions has been noted it may be found expedient to revalue the rainfall tests. It has been shown that unless soft, deionized, or distilled water is used, the results of simulated rainfall tests will be affected by the calcium and magnesium ions customarily found in hard waters.

## 12. Toxicity Tests

*John W. Meigs*

Toxicity tests of flameproof fabrics include evaluation of toxicity of the basic chemicals used, of the fabric at various stages of manufacture,

storage or shipment, and of the finished fabric as it will be used in field.

Toxicity of basic chemicals must be considered because certain ones highly poisonous even in small doses; repeated doses may cause cumu tive poisonous effects, or, in the case of flameproof fabrics, basic chemic might release poisonous substances under certain conditions of high te perature.

Toxicity of flameproof fabrics (including toxicity of solvents, dyes a finishes as well as basic chemicals) at various stages of manufacture, st age or shipment might adversely affect either civilian or military person in the Army's industrial or military installations.

Toxicity of the finished fabrics is primarily of concern to military p sonnel in the field.

Tests for determining toxicity of flameproof fabrics must be chosen cording to the particular phase of toxicity in question.

**Basic Chemicals.** Most of these are well known, as for instai borax, or ammonium phosphates. Experimental data on effects of ing tion, absorption by skin contact or inhalation of fumes are available in medical literature. In the case of untried chemicals, animal studies m be carried out to determine the minimum lethal dose by mouth, sub taneous injection, skin application or inhalation in the event that gases fumes are given off under conditions of high temperature. Life span te upon small animals, such as rats, may be necessary to determine whet chronic toxic effects may result. Fortunately, throughout the war it v not necessary for the Army to undertake any long-range research toxicity of basic chemicals in flameproof fabrics.

**Manufacturing Processes.** Toxicity tests are necessary at times determine the probable hazards to workers in industry. The haza usually encountered are inhalation of toxic fumes from open containers chemicals or skin contact with the flameproofing agent as a result of sp or splashes. In addition, there is the hazard of contact between finished flameproof equipment or material and the skin of personnel gaged in its manufacture or handling. Toxicity tests to determine hazards from fumes would have to be carried out upon animals unless d were already available. Spills or splashes are hazardous more often cause of the solvent involved than because of the flameproofing age However, this hazard could be estimated from knowledge of the toxicity the various basic ingredients. Finally there is the possibility that a wor may become sensitive to the materials contained in the flameproof substance. This would become apparent if any worker developed der titis and the causal relationship between the flameproofing agent and dermatitis could be proved by *diagnostic patch tests.* These tests, wh should be carried out by the plant physician or other qualified medi officer, would prove only that the particular individual was sensitive

the material in question and would not give any indication of the number of cases of dermatitis to be expected from use of the material over a long period of time. The technique of this test is similar to that described for the prophetic patch test.

**Finished Fabric.** The most important toxicity tests, however, from the military point of view are those used to determine whether a flameproof fabric is suitable for use by military personnel in the field.

If toxicity tests of basic chemicals have not been accomplished, the flameproofing agent or flameproofed fabric is disapproved. However, if there is reasonable evidence that the fundamental chemicals are not seriously toxic, tests are undertaken to discover whether the finished material will cause skin irritation to personnel using it under standard field conditions.

**Prophetic Patch Test.** The likelihood of development of skin irritation is commonly determined by the *prophetic patch test,* devised by Dr. Louis Schwartz and Dr. Samuel Peck, of the United States Public Health Service.[40] This method has been extremely useful throughout the war period in toxicological evaluation of fabrics of various kinds, including flameproof fabrics. A rather simplified description can be given as follows: The tests require about 200 subjects representing an average cross-section of the population; that is to say, no attempt is made to screen out persons who give a history of skin sensitivity to various substances unless such individuals are present in a percentage much greater than that which would be found in the population at large. Each material to be tested is cut into squares exactly 1 inch on a side. Areas on the back and arms of test subjects are designated as A, B, C, etc , up to the required number, and the materials are also listed as A, B, C, etc. Each patch is placed on the back or the arm in the designated area and is held firmly in place with a 3-inch square of adhesive with a 1.5-inch square of cellophane in the center to prevent direct contact between the patch and the adhesive tape. This assures that there will be a clear area of skin around the patch and that any reaction to adhesive tape will not interfere with reading of the test. After the patch has been left in place for 48 hours, it is removed, and the reaction is read 15 minutes after the adhesive tape has been taken off. Each preliminary reading is recorded, and 48 hours later a second reading is taken. The reason for the second reading is that redness caused by pressure from the patch or irritation from scratching may interfere with the proper reading of the results. After 48 hours these reactions will have disappeared, and any evidence of skin irritation remaining in the area with which the patch had contact will indicate definite irritation as a result of the patch itself. The subjects are then instructed to return after 6 to 10 days, and at that time patches duplicating the original set are placed in

[40] Schwartz, L., and Peck, S. M., Reprint 2252, *Pub. Health Reports,* 59, No 17, 546–557 (1944).

approximately the same positions as before. These tests are read c
the same way as the first series.

The first series of tests indicates the presence or absence in the or
patch of a primary skin irritant (a substance which will produce
irritation in practically anybody, the first time it is applied to the
for a short period). Strong acids or alkalies are typical examp
primary irritants. Almost any chemical in a high enough concent
will act as a primary irritant. The second series of tests indicates the
ber of individuals who have been sensitized to the particular chemic
the first test. For example, the chemicals in patch A may produce r
action the first time; however, during the 48 hours in which the patcl
contact with the skin they initiate chemical or physiological ch
within the skin, so that when it is applied the second time 6 to 10
later definite skin irritation results. Chemicals are extremely varial
their ability to cause such sensitization; for example, almost everyon
become sensitized quite easily to the irritant in poison ivy; howeve
tremely few people become sensitized to neoprene rubber or cellop
Some chemicals are so simple or their characteristics are such that it i
possible for them to cause sensitization.

In the interpretation of the results of these patch tests, great impor
is attached to the proposed end use of the particular product. For exa
if a flameproof fabric is to be used in tents, it is obviously of little c
quence whether it produces a small amount of irritation in human sul
when applied closely to their skin for 2 days. Such a contingency i
likely to arise under field conditions. It is therefore possible to app
for tentage a relatively irritating flameproof fabric. On the other han
it is desired to use a flameproof fabric in clothing, much more rigid st
ards apply. If it is anticipated that the clothing will come in intimate
tact with the skin of the neck or the body, it is desirable to select a
terial which gives no more than one reaction, and preferably a mild
in 200 subjects. This may not always be possible because such clo
must be used in certain situations regardless of whether it is some
irritating to the skin. It is obviously better to have a soldier with an
tated skin than one who has been badly burned. These decisions on t
ity require maximum cooperation between the technical personnel
cerned with development of the project and the medical authority ma
the decision. The latter must present the situation to the agency reque
the test, point out the desirability of using non-irritating chemicals
indicate which of the available samples of flameproof fabrics tested
the least irritating.

The greatest single problem in carrying out prophetic patch tests
been that of obtaining an adequate number of test subjects and retai
them for the 2 series required. Because the tests involve a certain am
of inconvenience, many subjects fail to return for the second series. S

the latter determines the probability of sensitization by the material in question, it is even more important than the first series. It is therefore highly desirable if results are to have optimum statistical significance to keep 200 volunteers throughout the test. Unfortunately this goal has only rarely been achieved, and results, although sufficient for a conclusion, have often not permitted unqualified approval of materials. It is believed that agencies requiring evaluation of materials by a patch test should consider supplying volunteers, since such agencies are often in a better position to arouse enthusiasm for the project than any other organization.

**Field Test.** An additional procedure for testing the finished fabric is the field test. This has not been used very widely to evaluate possible toxicity of flameproof fabrics. During wartime the method was limited in its usefulness because it was too time-consuming and the required professional and technical personnel were not available to carry out tests and record results in the detailed manner necessary for sound scientific conclusions. At present with neither time nor personnel at a premium this method, realistically carried out, should be used to augment the prophetic patch test and other means of evaluating toxicity of flameproof fabrics. Well-conducted tests with records kept by observers trained to recognize toxic skin reactions would go far to establish a better correlation between the results of patch tests of fabrics and the effect of their actual use.

In summary, toxicity tests of flameproof fabrics require consideration of basic chemicals, manufacturing processes and finished fabrics. Since data have usually been available about basic chemicals and manufacturing processes, the greatest amount of new work has been done in testing toxicity of finished fabrics. The possible skin-irritating properties of such fabrics have been of chief concern to the Army, and these have been evaluated in many cases by using the prophetic patch test. In the future, evaluation of toxicity of flameproof fabrics by accurate field test should supplement other methods.

## 13. Related Tests

*R. D. Wells*

### a. Water Repellency

Though the term "water repellency" is often misused, in the technical sense it relates solely to the hydrophobic nature of a material or surface as distinct from the more general property of "water resistance." The latter is a total effect dependent on both the repellent or non-wetting nature of the material and the impedance or blocking of flow of water by the material mass itself. The relationship of the several contributing factors involved in the complex system of fibers and yarns of a textile fabric is beyond the scope of this chapter. However, the common tests for water-

resistant fabrics are divided into simple categories in accordance w
two major factors mentioned above though the distinction may no
an absolute nature.

Of the repellency tests, the "spray" test[41,42] has had the longes
and still serves a useful control function in the finishing of a
material. A rating of repellency is assigned according to the amo
water observed to adhere to the fabric after a certain quantity of w
sprayed on it under standard conditions. The sample is mounted flat
a six-inch hoop and clamped on by a slightly larger hoop, then mou
a 45° angle to the horizontal with its center six inches under the
nozzle. The standard nozzle contains twenty holes 0.035 inch in
eter, connected to a conical funnel. For the test, 250 ml. of wa
poured quickly into the funnel and allowed to spray on the sampl
surface water droplets are then shaken off by tapping the sampl
mounted, once in each direction against a solid object. The amou
distribution of water adhering to the sample are compared visually
graduated series of standard pictures and assigned a rating of 0, 50,
80, 90, or 100 according to the designated rating of the picture most
matching the appearance of the sample. The 100 rating is the h
indicating no visible adhesion of water. A modification of this met
which the adhering water is weighed is included in A.S.T.M. stan

The dynamic absorption test[44] has become recognized as a better
ation of hydrophobic finishes than the spray test. A set of five w
8 by 8 inch samples is placed in 2 liters of water in a 6-liter hex
tumble jar, which is then rotated about a transverse axis at 55 R.P.
the end of a designated time interval the samples are removed a
individually through a standard wringer, once alone and once b
dry blotters. The water absorption is then determined by weighi
wet samples and comparing with the dry weight. This test may be
fied to attain an absorption rate by removing the samples at stated
vals until equilibrium is attained. It has an advantage in that it m
used for comparative purposes where the fabric samples are not of i
cal physical construction, though some reservations should be made
widely different fabrics are compared. It is a measure of the effi
with which the finish reduces the natural absorbency of the fabric,
dependent both on the inherent properties of the finishing compoun
the degree and uniformity of the application. It has further validit

[41] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalo
III, par. 5a(1)—CCC-T-191a.

[42] A.A.T.C.C. Tentative Method—Standard A.A.T.C.C. Test Methods, 1943
book, p. 236.

[43] A.S.T.M. Designation: D 583-40T; A.S.T.M. Standards on Textile M
(1944), p. 106.

[44] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog
III, Par. 5b(1)—CCC-T-191a.

test of value of the finish in that the motion of the sample in the immersion bath breaks down the false resistance to initial wetting caused by entrapped air, which in some other tests gives misleading evaluations.

The water-resistance tests in which the total effect of fabric and finish is measured are of two general types: hydrostatic pressure and simulated rainfall. Federal Specifications[45] and A.A.T.C.C.[46] and A.S.T.M.[47] standards outline the conventional hydrostatic pressure test in which the height of the steadily increasing column of water imposed on the sample is recorded when the water penetrates the fabric. The sample is clamped over a standard orifice, and the hydrostatic load applied by raising a connected reservoir with mechanical drive, or by a constant feed device, so that the level is increased at a rate of 1 cm. per second. The height of the column is then recorded at the time that the third drop of water appears at different places through the sample. This type of test has been widely used for many years though its applicability for many materials, particularly clothing fabrics, is subject to question. A percolation test[48] uses a similar apparatus except that the hydrostatic head is maintained at a designated level and the amount of leakage measured. Both tests are sensitive to the manner in which the hydrostatic load is applied, and to changes occurring within the fabric as the fibers swell in wetting out. For coated fabrics and other supposedly continuous films, however, those limitations do not apply. Such tests may also be the best adapted for evaluating the fabric without regard to hydrophobic finish provided that the hydrophobic forces are overcome either by a shock load or protracted time.

For clothing fabrics in particular the simulated rainfall tests are finding increasing favor. With the exception of the apparatus described in the Federal Specification,[49] and the Bundesmann apparatus used in European laboratories, the various rainfall devices have not reached a state of official standardization. As would be expected, however, being nearer to the natural conditions of usage, correlation with service tests has been more nearly approached. The main limitations to date are in providing the same dynamic forces in the drop impact as occur in nature without going to the approximately 20-foot free fall required to reach terminal velocity, and in presenting the sample to the shower in a realistic fashion as to shape, backing, and motion. It has been possible for the Army to

[45] Textiles; General Specifications, Test Methods—Fed. St'd Stock Catalog, Sect. IV, Par. 5c(1)—CCC-T-191a.

[46] A.A.T.C.C. Tentative Method—Standard A.A.T.C.C. Test Methods, 1943 Yearbook, p. 232.

[47] A.S.T.M. Designation: D 583-40T; A.S.T.M. Standards on Textile Materials (1944), p. 104.

[48] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. III, Par. 5c(2)—CCC-T-191a.

[49] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. III, Par. 5c—CCC-T-191a.

make use of full-scale rain rooms and outdoor rain courts, with wat drop size and distribution equivalent to natural rainfall in three rang of intensity from 0.1 inch per hour to 3 inches per hour. In such tests f garment fabrics, the garments are worn by human subjects traversing t rain area. However, these facilities are not readily available to m agencies, and dependence must be placed on one or more of the mo convenient procedures. The selection of the most applicable test meth should always be based on the following considerations: (*a*) the conditio of use or service for the material in question, and (*b*) the importance the finish, fabric, or total performance in the evaluation being made.

## b. Mildew Resistance

Many types of tests for mildew resistance have been proposed a practiced by research and procuring agencies. The differences are due part to the facilities available within each agency and the scientific bac ground of the personnel responsible, and in part to the type and expect use of the materials in which the individual agencies are most intereste The resulting confusion in evaluation standards has drawn the attenti of not only the procuring services but also the National Bureau of Stan ards, Federal Specification Board, National Defense Research Committe American Society for Testing Materials, and the American Association Textile Chemists and Colorists, all of whom have taken an active pa in the effort to resolve these different tests and establish generally reco nized procedures. As of this date, however, the effort has met only parti success, largely because of the difficulty in correlating any accelerate tests with the complex phenomena encountered in natural exposures.

A distinction is generally recognized, though admittedly vague, betwe "mildewing" and "rotting"; the former describing a visible growth fungus on the material in which tendering may or may not result, and th latter indicating microbiological attack on the material without regard t the extent of visible "mildew." In a relatively small class of material suc as camouflage garnishings, "mildew" as described above is the predomi nating consideration because of the effect on the color of the materia With most materials, however, the prevention of "rotting" is the aim the fungicidal treatment and the tests are meant to measure the efficien of this protection even though they are called in common usage "mildew resistance tests."

**Pure Culture Tests.** These tests are those in which the sample i inoculated with the spores of a specific fungus organism, placed in a war incubation chamber under high humidity conditions for a stated lengt of time, and evaluated either by visual evidence of fungus growth on th sample or the extent of damage in terms of breaking strength. The man variations lie in the choice of test organism from the hundreds whic

might be suggested, in the condition of the organism at the time of inoculation (spores only, or spores and flourishing hyphae), the mineral and organic nutrients supplied in the test, and the temperature and moisture conditions. An example of this type, which has probably had the longest and most general usage is the "Chaetomium globosum" test.[50] (Methods similar to this have been listed as tentative standards by A.S.T.M.[51] and soon will be listed by A.A.T.C.C.) Though in practice a visual examination of the incubated sample has often been used for the sake of convenience, the interpretation is in terms of rot resistance as Chaetomium globosum is known to be an active cellulose destroyer. An example where a superficial fungus (not an active cellulose destroyer) is used is the "Aspergillus niger" test for camouflage materials.[52]

Pure culture tests have the theoretical advantage of reproducibility, but are often criticized as being unrealistic due to the arbitrary choice of organism and conditions. A group of tests using either known or unknown multiple inoculum have been proposed as compromises between more natural conditions and reproducibility. An example of this type, in which part of the inoculum is derived from the soil, is the enriched soil suspension test.[53] It has been possible to obtain consistent results with this type of test within an individual laboratory, but correlation between laboratories has not been of a high order.

**Soil Burial Test.** This test, generally considered the most severe of the accelerated tests, is a direct contrast to the pure culture techniques. Samples are imbedded for a stated length of time in a warm soil rich in humus, and the loss in strength then measured. The inoculum here is a complex mixture of fungi and bacteria in all stages of development together with natural nutrients and probably enzymes produced in the microbiological action on other organic material in the soil bed Standardization is somewhat difficult because of differences in activity between soils from different sources or within any one soil bed from time to time, and its interpretation is further complicated by chemical or absorptive activity of soil components on fungicides or other finishing agents. The simplicity of procedure, however, recommends it in that it can be conducted without trained scientific personnel; while its severity is such that most materials and treatments which pass it will pass most other accelerated "rotting" tests currently used. On this latter point is based the common criticism that, by reliance on the soil burial test alone, some ma-

[50] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. VIII, Par. 1b—CCC-T-191a.

[51] A.S.T.M Designation D 684-42T; A S T M Standards on Textile Materials (1944), p. 100.

[52] U. S. Army Specification No. 39-13.

[53] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog, Sect. VIII, Par. 3—CCC-T-191a.

terials may be excluded which might be reasonably efficient under r
conditions of use. The procedure given in Federal Specification CC
191a,[54] is generally recognized, and is in general agreement with that
in A.S.T.M. standards.[55]

As in most technical fields, accelerated tests must be used with c
tion. It is common practice to use a variety of mildew-resistance t
evaluation of proposed materials or protective finishes, and select
which have given good performance in all tests. It is desirable wh
possible to conduct actual exposure tests of the material in the mo
treme climate (with regard to mildew conditions) and under the
severe conditions of service or storage which the material in qu
would be expected to undergo. If a certain treatment has been adop
this basis, it is then customary to check subsequent production c
treatment by a single test which is selected for convenience and its a
to detect faulty production of the supposedly standardized finish.

[54] Textiles; General Specifications, Test Methods—Fed. St'd. Stock Catalog
III, Par. 4—CCC-T-191a.

[55] A.S.T.M. Designation: D 684-42T; A.S.T.M. Standards on Textile Ma
(1944), p. 102.

# Chapter V

# General Flameproofing Processes for the Treatment of Cotton Fabrics

In addition to the evaluation procedures presented in the preceding chapter, those persons who are actively engaged in the development or application of flameproofing processes are, by necessity, also concerned with the nature of contemporary processes and the methods of industrial application. For the benefit of those readers, this chapter has been organized to present the chemical nature of the more common flameproofing processes, a discussion of the mechanisms by which they function, an examination of the laboratory experimentation upon which those mechanisms are based, and, finally, a practical description of the industrial practices employed in their commercial exploitation Obviously, each different flameproofing process cannot be considered individually. Thus, the available treatments have been grouped according to the general type of flameproofing agent and the method of impregnation, further separating the temporary water-soluble treatments from those of a more durable nature Since the water-soluble salts have, until recently, predominated the field of flameproofing, it is fitting that this group be considered first.

## A. TEMPORARY TREATMENTS

*Robert W. Little*

### 1. Nature of Retardants

The majority of the interest in flameproofing agents in the past has been concentrated upon the water-soluble retardants. Furthermore, perhaps due to the fact that inflammability is commonly considered a characteristic of organic materials, the investigations have, with few exceptions, been concerned with soluble inorganic salts. The protection afforded by these retardants has been classified as "temporary" since the mildest water leaching or even profuse perspiration in clothing completely destroys the efficacy of the treatment. In some cases the retardancy is seriously impaired by long-term exposure to elevated temperatures or high humidity. For this reason, these "temporary" treatments are ap-

plied with the idea of periodic reprocessing in order to maintain t
sired properties of flame and glow resistance. The flameproofing ag
be considered in this section are water-soluble inorganic salts whi
generally applied to the fabric by simple immersion in aqueous sol

In considering the innumerable water-soluble, inorganic compou
potential flameproofing agents it should be borne in mind that an
flammable material will exert an inhibiting action upon the flamin
glowing characteristic of a fabric if added in sufficiently great quan
The characterization of a substance as a flame or glow retardant
be based upon its efficient performance by way of one of the mecha
of Chapter III, rather than upon the inhibiting effect caused by the
dilution of combustible material with large amounts of an incombu
compound or mixture.

A brief examination of the literature on the subject of flameproofin
indicate that practically all the common inorganic salts have be
vestigated as possible flameproofing agents for cellulosic materia
attempt will be made here to present or discuss this group of comp
in its entirety. For a comprehensive survey of the salts and mi
which have been considered, the reader is referred to two of the
bibliographies on the subject of flameproofing.[1,2] These articles c
nearly 700 references on the subject including over 400 patents. A
tempt will be made in the following sections to point out the general
of compounds to be considered and the groups into which they mig
classified on the basis of their mode of action.

The efficiency of a compound or mixture as a flameproofing agen
be dependent upon its ability to impart to the fabric a high deg
resistance to both afterflaming and afterglow. As has been pointed
previous chapters, these two characteristics are quite different and
or less unrelated phenomena which take place by entirely different m
nisms. For this reason many of the better flameproofing agents fro
standpoint of prevention of afterflaming fail to impart any appre
degree of glow resistance to the fabric. Similarly, boric acid, which
of the better water-soluble glowproofing agents, possesses very little
ity to prevent the afterflaming of fabric. Indeed, there are very few
able inorganic compounds which are able to produce effective resis
to both afterflaming and afterglow. Outstanding examples of this
group are the ammonium salts of phosphoric acid.

[1] "Fireproofing of Fabrics." Ramsbottom, J. E., and Snoad, A. W., Second
of the Fabrics Coordinating Research Committee, Dept. of Scientific and Ind
Research (Great Britain), (1930).

[2] "Bibliography on Flameproofing" Akin, E W., Spencer, L. H., and Mac
A. R., *Am. Dyestuff Reptr.*, 29, 418, 445 (1940).

### a. Flame Retardants

The salts which function in the prevention of afterflaming may be divided into three general groups on the basis of the mechanisms by which they function. These mechanisms have been discussed fully in Chapter III where it was pointed out that some of the accepted theories of flameproofing rest on a more or less sound foundation of experimental data while others are based more on speculation and do not serve to explain adequately the action of flameproofing mixtures. In several cases the physical and chemical properties of the compound make it equally applicable to more than one mode of action. It is highly probable that in the majority of cases a flame retardant is effective due to its functioning by more than one mechanism.

**Group I.** The retardants in this group consist of salts or mixtures which, when heated, melt at relatively low temperatures and subsequently resolidify in the form of a solid foam produced by the evolution of decomposition products. These materials are effective due to the formation of this foam which is stable to heat and serves as a barrier between the fabric and the flame. The retardants are generally either highly hydrated salts possessing low melting points or mixtures of a low-melting compound with a highly hydrated salt. In some cases the hydrate may be replaced by a carbonate or similar salt which decomposes with the evolution of non-flammable gases. Typical examples of this group of retardants are the following:

Borax [$Na_2B_4O_7 \cdot 10H_2O$]
Aluminum Sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$]
Borax : Boric Acid (7 : 3) [$Na_2B_4O_7 \cdot 10H_2O : H_3BO_3$]
Borax : Boric Acid : Diammonium Phosphate (7 . 3 . 5)
[$Na_2B_4O_7 \cdot 10H_2O \cdot H_3BO_3 : (NH_4)_2HPO_4$]
Borax : Diammonium Phosphate (1 . 1) [$Na_2B_4O_7 \cdot 10H_2O : (NH_4)_2HPO_4$]
Sodium Phosphate : Boric Acid (1 : 1) [$Na_3PO_4 \cdot 12H_2O : H_3BO_3$]
Boric Acid : Diammonium Phosphate (1 : 1) [$H_3BO_3 : (NH_4)_2HPO_4$]

There are many more inorganic compounds and their mixtures which could be included in this group and the efficiencies of the retardants range from the most highly efficient of the water-soluble type to those which can hardly be classed as flame retardants. Of those listed above, the first two compounds, borax and aluminum sulfate, are much less effective than any of the mixtures which follow. Some mixtures which produce voluminous foams, when tested by heating the powdered mixture to 500° C., are found to be non-effective as flame retardants when applied to fabrics. Typical examples would be:

Sodium Carbonate : Boric Acid (1 : 2) [$Na_2CO_3 \cdot 10H_2O : H_3BO_3$]
Stannic Chloride : Boric Acid (1 : 1) [$SnCl_4 \cdot 5H_2O : H_3BO_3$]

In the first case the material remaining on the fabric after impregnat and drying is essentially sodium tetraborate. This is in agreement w the flame test data which indicate this mixture to be approximately eq to borax in its resistance to afterflaming.

In the second case it was found that the foam did not form until t mixture had been heated for some time at 400–500° C. It appeared, the fore, that the fabric had been consumed by flame before foam formati occurred.

The efficiency of a retardant of this group, then, will depend upon t extent to which the mixture satisfies the following requirements:

1. One component, at least, must decompose at a relatively low te perature (80–200° C.) with the evolution of large amounts of gaseo products ($H_2O$, $CO_2$, $NH_3$, $SO_2$, etc.).

2. The other component must melt at a low temperature near that which gas evolution begins. The mixture should form a uniform melt whi solidifies as decomposition progresses.

3. The foam formed as the evolved gases blow up the solidifying me must be formed at a low temperature, without long heating and be stab at temperatures as high as 500° C.

These flame retardants of Group I are generally the most efficient of a the water-soluble type in the prevention of afterflaming. At add-ons only 10 to 12 per cent these mixtures prevent any afterflaming and als reduce greatly the damage which the fabric suffers while in contact wit the igniting flame.

**Group II.** The flame retardants of this second group consist of inor ganic acids, acid salts or salts capable of liberating acids on heating. I general these flameproofing agents are less effective than those of Group in the prevention of afterflaming but have the advantage of being quit effective in the inhibition of afterglow. The following are representativ of this type of retardant:

Orthophosphoric Acid [$H_3PO_4$]
Monoammonium Orthophosphate [$NH_4H_2PO_4$]
Diammonium Orthophosphate [$(NH_4)_2HPO_4$]
Monosodium Orthophosphate [$NaH_2PO_4 \cdot H_2O$]
Sulfamic Acid [$NH_2—SO_2—OH$]
Ammonium Sulfamate [$NH_2—SO_2—O—NH_4$]
Ammonium Sulfate [$(NH_4)_2SO_4$]
Ammonium Molybdate [$(NH_4)_2MoO_4$]
Zinc Chloride [$ZnCl_2$]
Antimony Oxychloride [$SbOCl$]
Aluminum Sulfate : Monoammonium Phosphate [$Al_2(SO_4)_3 \cdot 18H_2O : NH_4H_2PO_4$]
Ammonium Sulfamate : Diammonium Phosphate [$NH_2—SO_2—O—NH_4 : (NH_4)_2HPO_4$

The efficiency of these compounds and mixtures in the prevention of afterflaming appears to be dependent upon the ability of the retardant to furnish a free acid group at the time of incipient flaming. The function of

this free acid in the prevention of afterflaming has been previously discussed in Chapter III. That this is the primary requirement of this group of retardants is illustrated by the relative efficiencies of orthophosphoric acid and its sodium salts. When the acid anhydride is balanced by an equivalent amount of alkali oxide in the combustion residue, the salt does not possess flame-retardant properties. Bearing in mind the formation of the pyrophosphate at approximately 200° C., the reactions on heating could be represented as follows:

$$A.\quad 2(Na_3PO_4 \cdot 12H_2O) \xrightarrow{\Delta} 3Na_2O \cdot P_2O_5\ (3{:}1) + 12H_2O\uparrow$$

$$(Na{-}O)_3P{=}O \xrightarrow{\Delta} \text{No change}$$

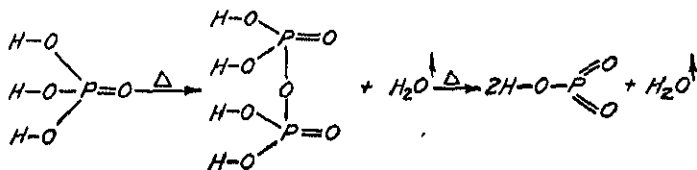
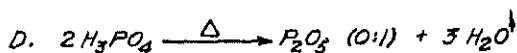
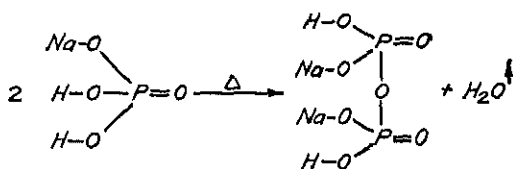
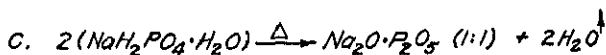
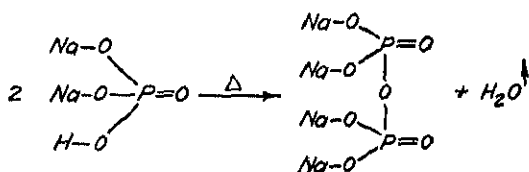
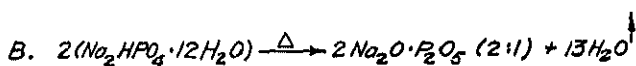
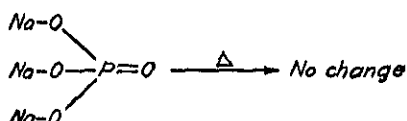
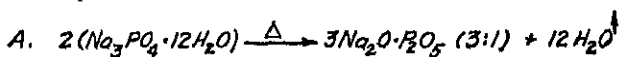
$$B.\quad 2(Na_2HPO_4 \cdot 12H_2O) \xrightarrow{\Delta} 2Na_2O \cdot P_2O_5\ (2{:}1) + 13H_2O\uparrow$$

$$2\ (Na{-}O)_2(H{-}O)P{=}O \xrightarrow{\Delta} (Na{-}O)_2P({=}O){-}O{-}P({=}O)(O{-}Na)_2 + H_2O\uparrow$$

$$C.\quad 2(NaH_2PO_4 \cdot H_2O) \xrightarrow{\Delta} Na_2O \cdot P_2O_5\ (1{:}1) + 2H_2O\uparrow$$

$$2\ (Na{-}O)(H{-}O)_2P{=}O \xrightarrow{\Delta} (H{-}O)(Na{-}O)P({=}O){-}O{-}P({=}O)(O{-}Na)(O{-}H) + H_2O\uparrow$$

$$D.\quad 2H_3PO_4 \xrightarrow{\Delta} P_2O_5\ (0{:}1) + 3H_2O\uparrow$$

$$(H{-}O)_3P{=}O \xrightarrow{\Delta} (H{-}O)_2P({=}O){-}O{-}P({=}O)(O{-}H)_2 + H_2O\uparrow \xrightarrow{\Delta} 2H{-}O{-}P({=}O)({=}O) + H_2O\uparrow$$

*Equations for chemical reactions; heating of sodium phosphates.*

The requirement of the presence of the free acid groups in order to function in the prevention of afterflaming is illustrated by the flame test data presented in Table 1.

Table 1. Relative Flame Retardancy of Orthophosphoric Acid and Its Sod
(45°-Microburner Flame Test)

| Compound | Add-On % | Afterflaming sec. | Char Area in² |
|---|---|---|---|
| $Na_3PO_4 \cdot 12H_2O$ | 77.5 | 3 | C.C.* |
| $Na_2HPO_4 \cdot 12H_2O$ | 57.4 | 60 | C.C. |
| $NaH_2PO_4 \cdot H_2O$ | 16.9 | 1 | 2.4 |
| $H_3PO_4$ | 14.8 | 0 | 2.5 |

* C.C.—Completely consumed by afterflaming and afterglow.

Trisodium orthophosphate does exhibit a slight flame retardai it is of low order and probably attributable to another mechanism that of the compounds of Group I. The disodium salt shows a more efficient action in slowing the burning rate but still could classified as an effective flame retardant. The monosodium salt acid itself are fairly efficient flame retardants as shown by the resi tained at the relatively low add-ons indicated.

The requirements for the members of this group will be clearer reader will refer briefly to the discussion of the dehydration ca mechanism of flame retardancy as discussed in Chapter III.

**Group III.** The third general group into which the soluble, in flame retardants may be subdivided consists of those compounds decompose or sublime on heating, evolving large amounts of non-i mable gases or vapors. The members of this group in general con carbonates, chlorides, ammonium salts and highly hydrated sa pointed out in the fundamental discussions of Chapter III, this nism of flameproofing by the generation of a non-inflammable atmo is not as credible nor as well substantiated as the other two and many of the compounds in this group have been, or might be, assig one of the other two groups. The following will serve as examples

Hydrated Sodium Carbonate [$Na_2CO_3 \cdot 10H_2O$]
Ammonium Chloride [$NH_4Cl$]
Ammonium Bromide [$NH_4Br$]
Ammonium Iodide [$NH_4I$]
Ammonium Sulfate [$(NH_4)_2SO_4$]
Ammonium Sulfamate [$NH_4O—SO_2—NH_2$]
Sodium Tungstate [$Na_2WO_4 \cdot 2H_2O$]
Trisodium Orthophosphate [$Na_3PO_4 \cdot 12H_2O$]
Calcium Chloride [$CaCl_2 \cdot 6H_2O$]

There are a few members of this group of compounds which, a cannot readily be assigned to either of the other mechanisms. Th standing examples are the ammonium halides. They exhibit no fo tendencies on heating alone and also very little decomposition to th responding halogen acids. It may be that they will fall into Group II more is known about the course of their thermal degradation reacti the presence of cellulose and its decomposition products. Extensive

ciation into ammonia and the halogen acid has been reported in the neighborhood of 350° C. but thus far the flame-retardant properties seem to be related more to the ease of sublimation and the amounts of sublimate formed.

It is possible that in many cases the flame-retardant action of a compound is enhanced by this formation of a non-inflammable atmosphere or dilution of inflammable gaseous products. This would seem, however, to be a secondary rather than a primary cause of flame retardancy.

### b. Glow Retardants

The water-soluble compounds which are effective in the prevention or inhibition of afterglow are limited almost entirely to boric and phosphoric acids and their acid salts. As was similarly pointed out in the discussion of flame retardancy, many compounds exhibit anti-glow tendencies but only at excessively high add-ons. This could be attributed to the great amounts of added material merely preventing oxygen from coming in contact with the carbonaceous char. Discussion of the mechanisms of afterglow in an earlier chapter have pointed out that true glow retardants are effective at exceedingly low add-ons and apparently function by catalytically influencing the oxidation of carbon.

The compounds of boric and phosphoric acids are effective in the prevention of afterglow only when the salt will decompose at flame temperatures or below to yield a free acid group. In cases where the acid anhydride is balanced by an equivalent amount of alkali or alkaline earth oxide the salt does not possess glow-resistant properties. A convenient example of this effect is orthophosphoric acid and its sodium salts. The reactions occurring on heating these compounds were discussed in the preceding section under the flame retardants of Group II. Employing similar data for illustrative purposes, the requirement of the free acid groups in order to function in the prevention of afterglow is clearly shown by the following flame test data.

Table 2. Relative Glow Retardancy of Orthophosphoric Acid and Its Sodium Salts (45°-Microburner Flame Test)

| Compound | Add-On % | Afterglow sec. | Char Area in.² |
|---|---|---|---|
| $Na_3PO_4 \cdot 12H_2O$ | 77 5 | 400 | C C.* |
| $Na_2HPO_4 \cdot 12H_2O$ | 57.4 | 70 | C C. |
| $NaH_2PO_4 \cdot H_2O$ | 16.9 | 0 | 2 4 |
| $H_3PO_4$ | 14.8 | 0 | 2 5 |

* C C.—Completely consumed by afterflaming and afterglow.

Similar data could be presented for boric acid and its sodium salts in which case borax not only does not exhibit any glow-resistant properties but instead seems to actually enhance the afterglow of untreated fabric.

Of the two principal glow retardants available the acid phosphat somewhat superior to boric acid. In combination with borax in an opt mixture, boric acid is unable to prevent afterglow. Similar mixtu borax and diammonium phosphate, on the other hand, render the completely glow resistant as well as flame resistant.

## 2. Methods of Commercial Application

Water-soluble flameproofing agents may be applied to fabrics by r of several different techniques. In any case the objective is to obta add-on which will be sufficient to render the material flame and glo sistant and to distribute the retardant uniformly throughout the f One factor which must be considered regardless of the impregnation nique used is the thermo-labile nature of the majority of flamepro agents. For this reason care must be taken in drying, mangling or ir the treated goods. Many of the more common retardant mixtures c water-soluble type will hydrolyze or decompose at temperatures bel near the standard ironing temperatures of 135–149° C. The mixtu borax and boric acid lose hydrated water at 127–134° C. and hence longed exposure to ironing temperatures will impair the effectivene the resultant treatment. Ammonium sulfamate and its mixtures with compounds decompose in the neighborhood of 134–147° C., depe upon the mixture, and release inorganic acid residues which will r the strength of the treated fabric. The ammonium phosphates are n serious offenders with respect to tendering but will lose ammonia, pa larly in the presence of large amounts of water, with the resulting fo tion of acidic residues and tendering of the fabric. In order to avoid u loss of either flameproofness or fabric strength, the mildest of drying ironing conditions must be employed. This may be accomplished by a ing the treated fabric to become fairly dry before ironing or mang High temperatures may be employed in pressing provided the wate be removed quickly and the fabric does not remain in contact wit iron or mangle long enough to reach the decomposition temperature commercial practice, where dry tumblers are used, the tumblers ca operated at medium temperatures and reduce the risk of loss of str or retardancy.

The four common methods of applying water-soluble retardants a immersion, spraying, brushing or impregnation in a commercial wa Because of the great variation in the chemical and physical properti different flameproofing agents the details of any impregnation techn will vary from one case to another. For this reason no specific metho be outlined which will be applicable to all retardants. An attempt wi made, however, to discuss in the following pages the general metho treatment. The application of these methods for a specific case will de

upon the solubility, minimum effective add-on, and similar properties peculiar to the flameproofing agent being considered.

### a. Immersion

The dipping of fabrics or garments into a volume of retardant solution followed by hand or roll wringing is the simplest method of application and is adaptable for treating small batches of material in the home. It has one advantage in that it tends to produce a more uniform distribution than can readily be accomplished by means of spraying or brushing. A convenient method of home impregnation is to incorporate the proper amount of flameproofing agent into the final rinse of the laundering procedure. In the case of many of the common commercial preparations this would be approximately one pound of retardant per gallon of water. The final dry add-on required in most cases ranges from 10 to 15%. If the fabrics dipped into the retardant rinse are very wet, the concentration of the solution will have to be greater than given above.

The adaptation of hand dipping to commercial impregnation where large quantities of material are being treated is quite slow and costly. The fabrics should be dried previous to impregnation which introduces an additional drying operation into the usual laundering procedure. In addition, the extra handling increases the labor requirements and considerable retardant is lost in transferring the fabric from tank to extractor.

### b. Spraying

In many instances it is advantageous to apply the flameproofing agent to a textile article without removing the article from service. This is particularly true in the case of interior decoration textiles such as drapes, curtains and buntings. The same method is applicable for rugs and slip covers and could be employed for any textile product. The fabric is hung up and sprayed with a highly concentrated retardant solution. Any suitable spraying equipment may be employed provided the spray is not too coarse. The fabric is thoroughly and evenly sprayed until it appears definitely moist. In order to avoid streaking of the fabric on drying the spray should be as fine as possible. With heavier fabrics it is often necessary to apply the spray to both sides of the cloth. This method tends to produce uneven distribution and requires some experience to achieve a satisfactory treatment. In treating curtains and garments in the home a modification of this technique can be used by applying the retardant when sprinkling the fabrics just prior to ironing. The cloth must be thoroughly moistened, however, and as pointed out previously, the fabric should be allowed to become nearly dry before ironing in order to avoid undue decomposition of the flameproofing agent.

### c. Brushing

In the event that a suitable spray gun is not available, a conc solution of retardant may be brushed onto the fabric. Again, care taken to moisten the fabric sufficiently and yet achieve a uniform tion in order that the treated material will not have a streaked o appearance.

### d. Commercial Laundry Treatment

Where large quantities of clothing or other piece goods are co the only effective and, at the same time, economical method of a flame-retardant treatments is by mechanical means. The pla equipped to carry out the impregnation is the commercial launc since the fabrics generally are laundered prior to treatment, a sa both time and expense is accomplished by impregnating at the t fabrics are washed. This type of treatment has been carried out c cially and shown to be practical. The variables which exist and the they exert upon the finished garment are presented in the following

In an investigation of the suitability of Army mobile laundry ment for the application of water-soluble flameproofing agents to h bone twill coveralls, the Quartermaster Board at Camp Lee, Virgin ried out a series of experiments using the standard mobile l equipment to apply a water-soluble retardant to combat clothin flameproofing agent used was a commercial preparation of the sulf phosphate type. The equipment and laundering procedures employe very similar to those used in commercial laundry practice. The was a standard 30 by 30 inch wash wheel which rotated at a speed of 30 revolutions per minute and reversed direction every 7 or 8 rot The 20-inch centrifugal extractor rotated on a vertical axis at a sp approximately 1600 revolutions per minute and accommodated ab pounds of clothing. The clothes were dried in dry tumblers of the st open-end type which were 36 inches in diameter and 30 inches lon laundering procedure employed was the standard mobile laundry p which may be briefly described as follows:

**Washing.**

| Load | Type of Solution | Water Level in Washer (in.) | C |
|---|---|---|---|
| Approx. 60 lbs. | break suds (1.5 oz. soap) | 8 | |
| of clothing | break suds (1.5 oz. soap) | 5 | |
| per run | rinse | 9 | |
| | rinse | 9 | |
| | rinse (3 oz. sour) | 9 | |
| Total. . . . . . . . . . . . . . . . . . . . . . | | | 1 |

The temperature is maintained between 90° and 100° F.

**Extraction.** Approximately 70% of the water is removed from the garments by spinning for 5 minutes. One half of the wash load, or approximately 30 pounds, is extracted at one time.

**Drying.** The extractor load is placed in a dry tumbler for 14 to 20 minutes depending upon climatic conditions and the efficiency of the plant.

Attempts were made to apply the flameproofing agent by including it in the final rinse of the regular laundering process and also by adding an additional rinse after laundering but prior to extraction. This approach led to inconsistencies in the percentage impregnation obtained and in some cases the add-on was below the minimum requirement of 11% ± 1. Consistent add-ons were obtained by applying the retardant in an additional rinse following extraction. Experimentation indicated that with insufficient volume of solution in the washer the garments were not effectively impregnated even after rotation for as long as 15 minutes. A minimum water level of 4 inches was found to be necessary to insure complete penetration of the entire load.

No appreciable saving of the flameproofing mixture was noted in drying the garments prior to treatment. Avoiding this additional drying step was very advantageous since the added process of tumbling the clothing after laundering and prior to immersion in the flame-retardant solution added 20 minutes to the operation. Furthermore, the omission is a distinct advantage in a commercial plant where drying is one of the major problems.

In the extraction process following the flameproofing treatment it is desired to remove the majority of the solution from the fabric leaving a wet pickup of approximately 100%. In the experiments at Camp Lee a constant concentration of solution was used and the wet pickup varied by means of varying the time of spinning in the extractor. It was found that the extraction time was the prime factor in obtaining the desired dry add-on of 11% ± 1. The relationship between extraction time and dry add-on is shown graphically in Figure 1, which indicates that the add-on may range from 17.1 to 34% depending upon the duration of the extraction period. In this particular case, using a solution concentration of approximately 10%, an extraction time of 10 seconds was optimum for producing a 100% wet pickup and correspondingly dry add-on of 10%. It is believed that in employing a similar process in a commercial laundry plant it would be preferable to maintain a constant rate of spinning or extraction time and adjust the pickup by variations in solution concentration. This is desirable since a slight variation in concentration in that case would not be nearly as critical as a variation in the extraction time as indicated in Figure 1. It is true that in some instances it may be necessary to vary the extraction time due to the solubility limitations of the particular flameproofing mixture used.

As a desirable economy in any commercial application it would be necessary to reclaim the used retardant solution. It was found in the course of the Camp Lee experiments that satisfactory impregnation could be at-

tained by returning the reclaimed solution to the washer in sufficien amount to give the minimum 4-inch water level. Due to the dilutio caused by the unextracted water in the garments, it was necessary to ad a booster of the compound occasionally. The concentration of the re tardant solution was readily checked by means of a hydrometer and specific gravity table could be prepared for the particular compound o mixture used and serve in estimating the size of booster required. In th course of routine treatments by this type of procedure the amount of re tardant required to renew the used solution could probably be determine on the basis of a few preliminary runs and remain essentially the sam

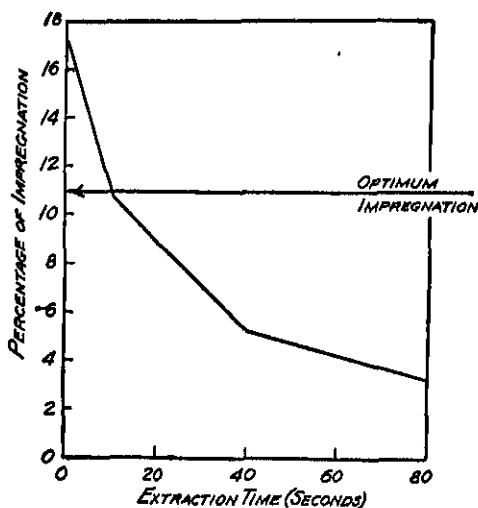



Figure 1. Relation of extraction time to percentage of impregnation. (Based on 28 pounds of retardant in a 4-inch water level.)

for subsequent treatments. A hydrometer reading would serve as a check of effective solution concentration.

Some of the available, commercially prepared, water-soluble flameproofing agents are quite acidic in nature and upon hydrolysis will exert a corrosive action upon equipment constructed of galvanized iron, copper, brass or bronze. Whenever possible, equipment made of stainless steel, lead, black iron, ceramic ware or wood should be used. In the event that the only equipment available is galvanized iron or one of the other metals which are subject to corrosion, it is necessary to flush out the washer and extractor after use. Washers made of galvanized iron were employed in the experiments described above and when properly flushed after use there were no signs of corrosive action on any of the laundry equipment.

As a result of the experiments described, the following technique was arrived at for flameproofing jackets, trousers and coveralls of 8.5-oz. herringbone twill. As was mentioned earlier the use of another flame retardant might necessitate a change in specific details such as the amount of compound used.

1. A wash-wheel load of clothing (55 to 60 lbs.) is first laundered ac-

cording to the process previously described (2 suds and 3 rinses). Time—19 minutes.

2. The laundered clothing is then extracted for 3 minutes per 30-pound load. Time—6 minutes.

3. The washer is drained and capped. Time—3 minutes.

4. 28 pounds of the flame-retardant compound is placed in the washer which is filled to the 4-inch level and rotated for 5 minutes. Time—5 minutes.

5. The garments are placed in the washer, the water level readjusted to 4 inches and the washer run for 5 minutes. Time—6 minutes.

6. The clothing is extracted for 10 seconds per 30-pound load. (Centrifugal time is taken from the instant the starter button is pushed until the instant the stop button is pushed. The extractor is then slowed down and stopped by means of the foot brake.) Time—3 minutes.

7. With a setting of medium on the tumbler the clothing is tumbled until dry. Time—60 to 70 minutes.

8. The washer is drained, the solution reclaimed, and the washer flushed. Time—10 minutes.

The total time of operation for this technique, including the laundering, amounts to from 112 to 122 minutes. It is very probable that this time could be reduced somewhat using a permanent installation in a commercial laundry.

As an illustration of the possible adaptations of this type of process to commercial laundry practice, a flow sheet of a flameproofing technique for use with water-soluble flame retardants is presented in Figure 2.

## B. DURABLE TREATMENTS

In recent years, the balance of interest in flameproofing treatments for textile materials has been centered upon those processes which display a greater or less degree of permanence. This has been heightened by the adaptation of flameproofing methods to commercial finishing practices and by the impending restrictions of the sale of hazardously inflammable fabrics. The three outstanding examples of durable flameproofing processes are thoroughly discussed in the following pages. The separation into the three general types shown was based partially on the nature of the flameproofing components themselves and, in part, upon the specific application techniques employed in industrial processing.

### 1. Urea-Phosphate Type

### a. Fundamentals of Processes

*S. Coppick and William P. Hall*

#### (1) *Reaction Mechanisms*

From purely fundamental considerations, the mineral acids have been shown to be singularly effective in inhibiting the combustion of cellulose.

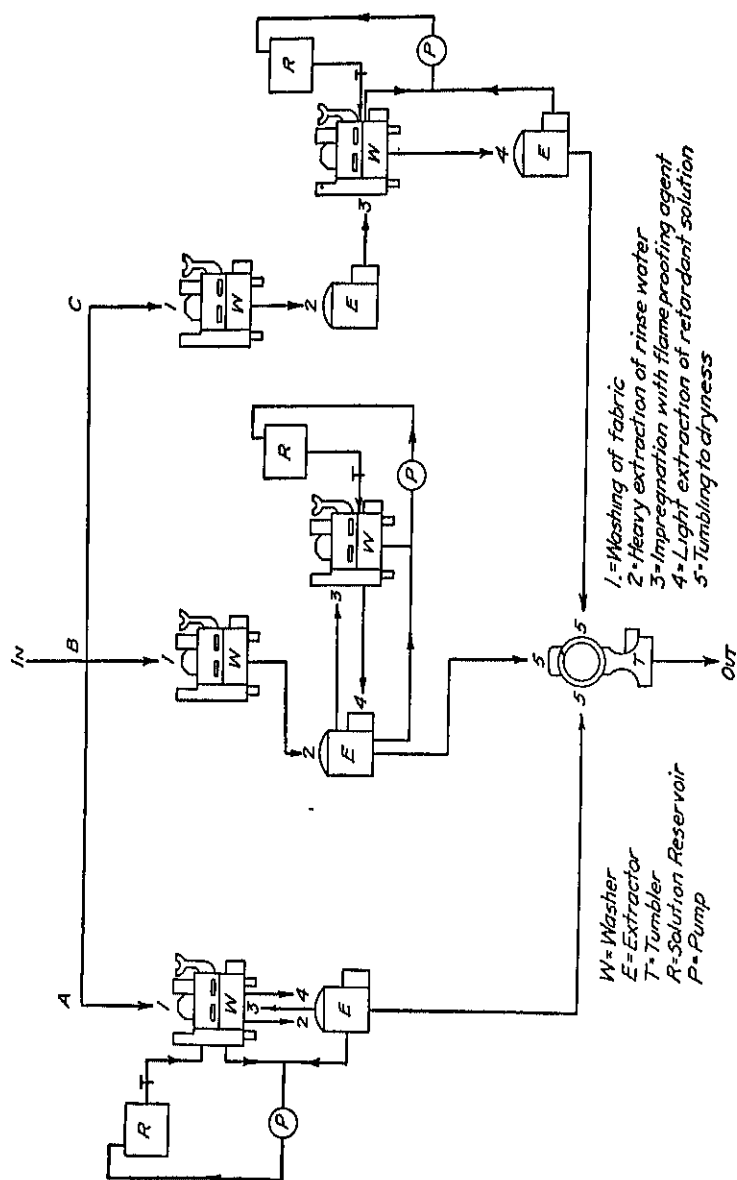



Figure 2 Flow sheet of the application of water-soluble flameproofing treatments in the commercial laundry installation.

This has led to considerable experimentation in the development of practical methods of adding these acid components to cellulosic materials. The addition of the simpler salts has already been discussed under "Temporary Treatments" in Section A of this chapter. In addition to the ammonium salts we may mention here other salts of organic bases such as urea,[3,4] alkylolamines,[5] guanidine,[6] and dicyandiamide.[7,8] The advantages of the amino or amido forms over the simple acid lie in the reduction of degradation through a buffering action and the ease of condensability to form complexes of lesser solubility.

Since the protection afforded by this type of treatment is primarily temporary in nature, attempts have been made to increase the permanence either by binding the acid or nitrogen-salt radical indirectly to the cellulose via resin condensation[9,10] or by direct chemical combination with the cellulose itself. The acidic constituents in the former case may be sulfates, borates, or phosphates, while in the latter case the sulfates and phosphates are usually employed. From practical considerations the phosphates have been shown to be most effective in promoting the desirable flame and glow resistance in the treated fabric.

The heating of cellulose in the presence of an acidic substance together with a hydrogen acceptor and a swelling medium is well known to favor esterification and the existence of cellulose phosphate has been reported quite frequently in the recent literature.[11,12,13,14,15,16] In general the reactions involved in the formation of the phosphate ester are impractical for flameproofing considerations due to the excessive degrading influence exerted on the fabric and the difficulty in adapting the solutions and methods used to commercial processes.

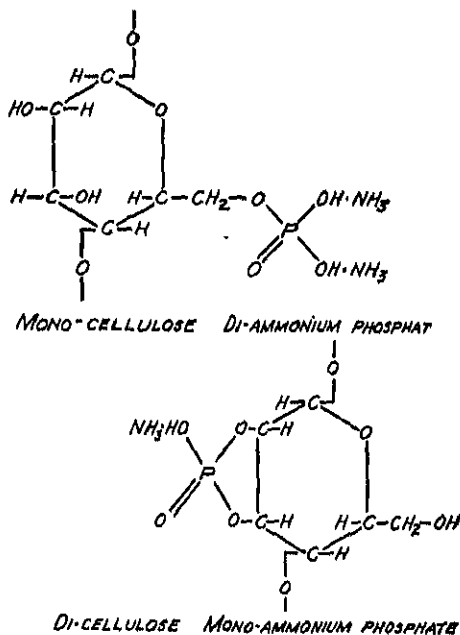
Recently, however, processes have been developed in which formation of the cellulose ester or nitrogen salt may be accomplished under conditions which are commercially practical and which do not excessively impair or destroy the fibrous properties of the cellulose.

Essentially, these processes involve treating the fiber at elevated temperatures with a mixture of an acid with a nitrogen compound. Under

[3] Boller, E R., U S. Pat. 2,097,509 (Nov. 2, 1937).
[4] Cuppery, M. E, U. S Pat. 2,212,152 (Aug 20, 1940).
[5] Whitehead, W, U. S. Pat. 2,032,605 (Mar. 3, 1936).
[6] Rosser, C. M, U S Pat. 2,305,035 (Dec 15, 1942).
[7] Triggs, British Pat. 476,043 (Oct. 31, 1936).
[8] British Pat. 486,766 (June 7, 1938).
[9] Groebe, F, U. S. Pat. 2,089,697 (Aug. 10, 1937).
[10] Thomas and Houston, British Pat. 446,379 (Apr. 29, 1936).
[11] Dreyfuss, C, U. S Pat. 1,837,150 (Dec 15, 1931)
[12] Champetier, G., *Compt. Rend.*, **196**, 930 (1933); *Ann. Chim.*, **10**, **20**, 5 (1933).
[13] Tanner, W. L., U. S. Pat. 1,896,725 (Feb 7, 1933).
[14] Hagedorn, M., and Guehring, E., U. S. Pat 1,848,524 (Mar. 8, 1932).
[15] I. G Farbenindustrie Akt.-Ges., German Pat. 547,812 (June 2, 1930).
[16] I. G. Farbenindustrie Akt.-Ges., German Pat. 556,590 (June 4, 1930).

these conditions a combination takes place between the three constituents and a complex cellulose ester is formed. This imparts durable flame-resistant properties to the cellulose. The most convenient means for carrying out this reaction is first to immerse the fabric in an aqueous solution containing the acid and the organic base. After drying, the material is cured at elevated temperatures where the esterification proceeds and finally the fabric is washed to remove the excess and unreacted components. It is, of course, impossible to apply a strong inorganic acid to cellulose and

MONO-CELLULOSE DI-AMMONIUM PHOSPHAT

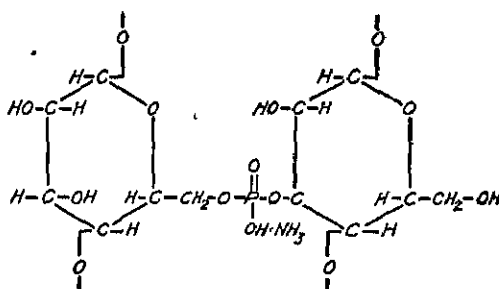
DI-CELLULOSE MONO-AMMONIUM PHOSPHATE

*Molecular formulae for mono-cellulose di-ammonium phosphate and di-cellulose mono-ammonium phosphate.*

then to cure for prolonged periods of time at the temperatures required for esterification without completely distintegrating the fiber. It appears, however, that if a large excess of certain nitrogen compounds such as urea are present, the degradation is greatly reduced. Moreover, it also appears that the presence of the urea creates conditions which favor the esterification reaction.

Actually, the esterification takes place in a molten solution of the nitrogen compound containing the acidic component. Hence, at the temperatures employed anhydrous conditions exist and the removal of the water of reaction proceeds under favorable conditions. Although the constituents

are most conveniently applied from aqueous solution and dried on the fabric, the direct procedure of treating the cellulose with the molten solution leads to similar products.

The reaction of cellulose with acid phosphates in the presence of a nitrogen base may be presumed to occur as illustrated on page 182, to give the mono- or di- substituted ester existing as the nitrogen salt, which for convenience is illustrated as ammonia.

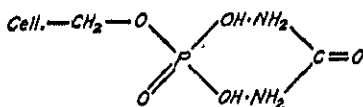
The mono-substitution may take place on either of the three available hydroxyls, but the primary (6) position should be the most readily esterified. With the di-substituted product the possibilities include reaction in the (2, 3) position as shown above, as well as between any one of the available hydroxyls on one cellulose chain together with another hydroxyl on a neighboring chain, *i.e.*:

*Molecular formula for cross-linked di-cellulose phosphate.*

The analysis of a typical permanently flameproofed fabric is given in the following table:

| | |
|---|---|
| Nitrogen: | 2.48% |
| Calculated as urea | 5.31 |
| $H_3PO_4$: | 8.78 |
| Calculated as urea-phosphate | 14.1 |
| Add-on: | |
| Determined | 16.0 |
| Calculated as urea-phosphate | 16.4 |
| Mole ratio: | |
| $H_3PO_4$ : urea | 1.01 : 1 |
| $C_6H_{10}O_5$ : $H_3PO_4$ | 5.92 : 1 |

This corresponds to an average degree of phosphation of about one ester group per 6 glucose anhydride units along the chain. The mean degree of substitution is hence about 0.16, but it should be pointed out that the reac-

tion is probably very far from homogeneous and high degrees of
tion will predominate in the more reactive locations on the fil
differences in morphological and fine structure.

The nitrogen content corresponds to two atoms of nitrogen pe
phosphorus, and may be presumed to occur as either the cellul
monium phosphate or the cellulose urea phosphate, *i.e.:*

*Molecular formula for cellulose urea phosphate.*

## (2) *Reaction Variables*

The practical formulations employed in these types of reactior
considerably more complex than those illustrated above; how
general system involves:

a. The cellulose.
b. The polybasic acid.
c. The salt-forming base.
d. The swelling anhydrous reaction media.
e. The buffer for the reaction.

In the simple system composed of phosphoric acid and urea,
component serves the three functions listed in c, d and e. The
considerations may be given to the influence of variations in ea
constituents in more complex systems.

### (a) *Fabric Reactivity*

The state of reactivity of the cellulose itself naturally domi
ease, extent and uniformity with which the esterification proce
well-known factors influencing this activity are the kiering, desi
mercerizing processes, all of which tend to produce a more recept
lose. Difficultly removable warp sizes or poor desizing pretreatn
pears either to retard the esterification or at least decrease it
geneity.

### (b) *The Acidic Component*

The acid constituent is preferably polybasic, which is in gener
ment with the theories for the interchain bonding mechanism. T
available acids meeting these specifications are those of phosph

sulfur, the former being the most efficient. It appears to be immaterial whether or not the original acid is in the higher or lower valance state so that metaphosphoric, orthophosphoric, pyrophosphoric, polyphosphoric, orthophosphorous and pyrophosphorous all behave similarly. However, orthophosphoric is usually employed. Since the reactive solution of the acid is sometimes prepared at elevated temperatures, and the esterification procedure itself is conducted between 150 and 200° C., the actual acidic component entering into the reaction with cellulose may not necessarily be that added as the primary component.

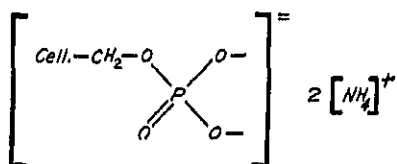
Substitution products of these acids may be employed provided that the substitution radical is of such a nature that it does not impair the rate of the esterification or reduce the hydrophilic nature of the ester. In general the introduction of groups of high carbon content reduces the efficiency of the acid as exhibited by the inferior protection afforded by fabrics prepared with either ethyl or phenyl phosphoric acid. Similarly, boron-substituted phosphoric acids lead to inferior products. Furthermore, it appears advisable to avoid unstable halogen-substituted phosphoric acids due to the excessive degradation encountered during curing or subsequent storage of the fabric. Thus fluorophosphoric is preferred to chlorophosphoric as the acidic component.

The hydrophilic nitrogen substitution products of the acids appear to be quite as satisfactory as the free acid itself. In any case the reactive mixture consists of an acid and a nitrogen base, and the acid does not exist entirely in the free state, but as the un-ionized salt in equilibrium with the corresponding ions. For example, diammonium orthophosphate, urea orthophosphate or guanidine pyrophosphate may be used in part or entirely in place of the acid. Similarly the amido acids such as phosphamic or the so-called nitride hexaphosphoric are effective. The exact constitution of many of the nitrogen-containing phosphoric acids is still a controversial subject and many acids of unknown constitution may be formed by reacting together the acid, its oxide or oxychloride and nitrogen-containing compounds at elevated temperatures. These acids also are effective.

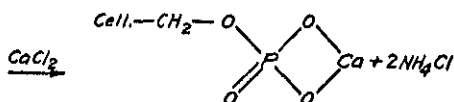
Metallic substitution products of the acids are generally considerably less efficient in their protective action than the free acid itself. For example, monosodium orthophosphate gives fair results while disodium and trisodium orthophosphate result in poor retardancy. Similarly, phosphates of the dibasic metals such as calcium and magnesium result in products with no appreciable flame resistance.

### (c) *The Salt-Forming Base*

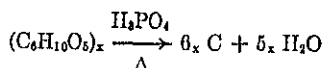
The effect of these various changes in the acid is readily explained on consideration of the ionic nature of the resulting ester salt. All of these structures are ionized salts and are more correctly represented as,

$$\left[ \text{Cell.}-CH_2-O-\overset{\overset{O}{\|}}{P}(-O^-)_2 \right]^{=} \; 2\,[NH_4]^+$$

*Molecular formula for ionized ammonium salt of cellulose phosphate.*

and are capable of exchange with a metallic ion as follows:

$$\xrightarrow{CaCl_2} \text{Cell.}-CH_2-O-\overset{\overset{O}{\|}}{P}\begin{matrix} O \\ O \end{matrix}\!\!>Ca + 2NH_4Cl$$

*Molecular equation for formation of calcium salt of cellulose phosphate.*

The resulting calcium salt is stable at flame temperatures and w
produce phosphoric acid when heated, as will the ammonium sal
flameproofing mechanism whereby cellulose is dehydrated on heat
promote formation of non-flaming products is thus destroyed by t
exchange with alkaline earth metals. The proposed dehydration
proofing mechanism may be represented as

$$(C_6H_{10}O_5)_x \xrightarrow[\Delta]{H_3PO_4} 6_x\, C + 5_x\, H_2O$$

rather than the normal decomposition whereby inflammable tar
gases are produced.

Similarly the interchain bonding capacity of the phosphate r
would be destroyed by replacement of the strongly hydrophilic car
or amino groups with hydrophobic groups or metals not capable of f
at flame temperatures. The facts then are also in accord with this f
proofing mechanism as proposed by Sisson [17] and previously outlin
Chapter III. Some phosphated fabrics behave typically as ion-exc
complexes, and may be conducted through a series of successive
ments whereby the protective qualities are lost and regained by add
or removal of the appropriate ion as shown below. These reactions
be illustrated as:

[17] Sisson, W. A., Paper presented at Industrial Advisory Panel Meeting on F
proofing, N.R.C. Project Q.M.C. # 27, Office of the Quartermaster General,
ington, D. C. (1945).

Cell.—$CH_2$—O—P(=O)(OH·$NH_2$)(OH·$NH_2$)C=O $\xrightarrow{CaCl_2}$ Cell.—$CH_2$—O—P(=O)(O)(O)Ca

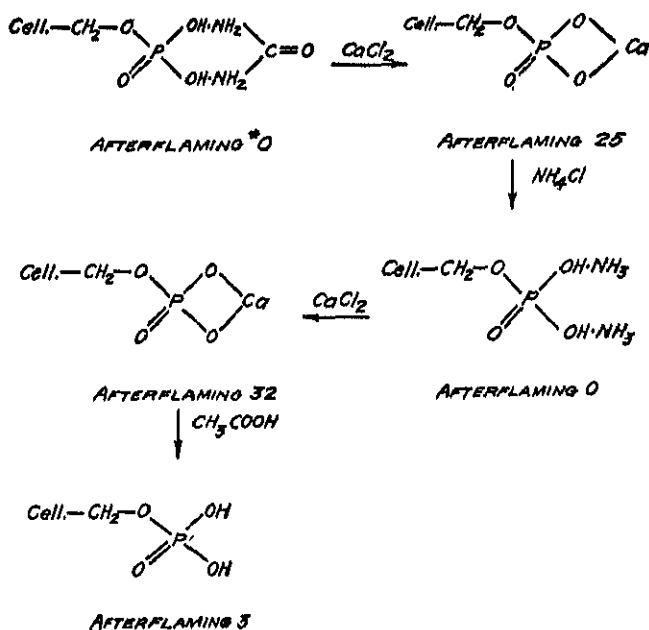
AFTERFLAMING *0 AFTERFLAMING 25

↓ $NH_4Cl$

Cell.—$CH_2$—O—P(=O)(O)(O)Ca $\xleftarrow{CaCl_2}$ Cell.—$CH_2$—O—P(=O)(OH·$NH_3$)(OH·$NH_3$)

AFTERFLAMING 32 AFTERFLAMING 0

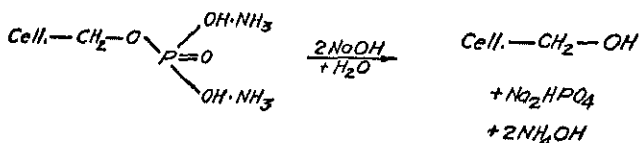
↓ $CH_3COOH$

Cell.—$CH_2$—O—P(=O)(OH)(OH)

AFTERFLAMING 3

*AFTERFLAMING IN SECONDS VIA THE 45° MICROBURNER FLAME TEST.

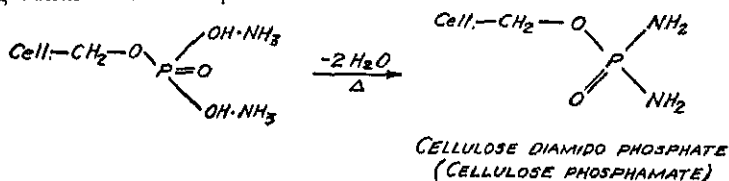
*Molecular equations depicting ion-exchange reactions with $CaCl_2$*

These hypotheses would explain also the instability of some phosphated fabrics to sea water and very probably account for the loss of fireproofing qualities during laundering with ionic detergents. With strongly alkaline detergents, however, the action most probably is mainly saponification, *i.e.*:

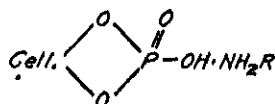
Cell.—$CH_2$—O—P(=O)(OH·$NH_3$)(OH·$NH_3$) $\xrightarrow[+H_2O]{2NaOH}$ Cell.—$CH_2$—OH + $Na_2HPO_4$ + $2NH_4OH$

*Molecular equation for saponification of cellulose ammonium phosphate*

The prolonged heating of ammonium salts favors the formation of the non-ionic amide. It is hence proposed that increased stability by suitable curing conditions takes place as follows:

Cell.—$CH_2$—O—P(=O)(OH·$NH_3$)(OH·$NH_3$) $\xrightarrow[\Delta]{-2H_2O}$ Cell.—$CH_2$—O—P(=O)($NH_2$)($NH_2$)

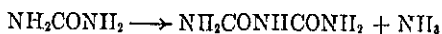
CELLULOSE DIAMIDO PHOSPHATE
(CELLULOSE PHOSPHAMATE)

*Molecular equation for formation of amide on heating via dehydration.*

This latter structure should be stable to media such as sea wa
ionic laundering conditions, etc., but still should be susceptible t
fication by strong alkali.

By appropriate formulation of the treating solution and by
curing conditions the tendency towards ionic reactions of the ty
trated above may be decreased, quite appreciably. Besides the ar
mation as previously discussed, there exists the possibility of caus
condensations to occur with the nitrogen salt radical to render it i
Furthermore, the use of more complex amines or amides to inc
molecular size of the side group should also decrease diffusion a
rates of exchange. These types may be illustrated as:

*Type formula for complex cellulose phosphate amides and amines.*

where $R$ may be considered as an $-\text{N}-\overset{\text{O}}{\overset{\|}{\text{C}}}-$ complex. The i
nitrogen to phosphorus ratio in the more permanent fabrics disc
the following sections illustrates this behavior.

The nitrogen base used in the treatment controls the type of
salt of the cellulose ester. However, since the curing conditions n
be above dissociation and condensation temperatures, the result
may not be that of the original base. For example, in processes i
urea, the following proceeds during curing:

$$NH_2CONH_2 \longrightarrow NH_2CONHCONH_2 + NH_3$$

Thus we have the possibility for formation of either the urea, b
ammonium salt. Moreover, in complex systems involving severa
the number of possibilities are enormous and the system becom
complicated. Further complications are introduced when one consi
number of possible combinations and condensations which can o
heating, say, urea and guanidine in the presence of anhydrous pho
acid. Moreover, on the final washing of the cured fabric, ion excha
occur and in the limit the final structure will probably be determ
the most stable of the salts present and its concentration at th
surface.

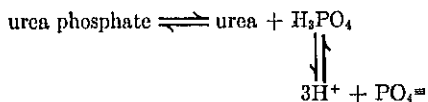
### (d) *The Reaction Medium*

To carry out the reaction at the temperature required for the est
tion a medium is necessary. The requirements for this are that it
be a solvent for the acid component and a swelling agent for the ce

That is, it should distend the disordered regions of the network to an extent at least equal to that produced by water and transport the esterification agent into the fiber. The medium should be fluid in the anhydrous state at temperatures above 140° C. and as far as possible should be chemically inert towards cellulose. Moreover, it should not decompose readily at curing temperatures to give highly basic or acidic substances for obvious reasons. The substances which come closest to satisfying all these requirements are the weak nitrogen bases with strong hydrogen bonding groups. These groups must be stronger than the mutual attraction between the cellulosic hydroxyls which naturally leads to the choice of the $>C{=}O$ and $-NH_2$ radicals. Thus the reaction proceeds in the presence of formamide, acetamide, urea, biuret, dicyandiamide, or melamine. Substitution products of these weak nitrogen bases may be used as media provided the substitution does not destroy or reduce their hydrophilic or hydrogen bonding power. Halogen, alkyl or aryl substitution products appear to be unsatisfactory as exemplified by the relatively poor performance of methyl urea. Moreover, the weak basic character of the media should not be altered by the introduction of amino or hydroxy groups as, for instance, in imino-urea (guanidine) which develops strong basic characteristics in the process.

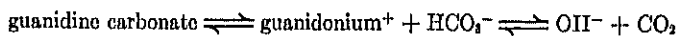
### (c) *The Reaction Buffer*

The esterification appears to proceed most satisfactorily under acidic conditions, but these are also the conditions under which hydrolytic degradation ensues with unfavorable strength losses. Moreover, as pointed out in Chapter II, in the alkaline range oxidative processes occur which are equally detrimental to the physical properties of the final product It is obvious therefore that the reaction should be carefully buffered at optimum conditions which favor a sufficiently rapid esterification with a minimum degradation. Of all the substances which appear to protect cellulose at high temperatures, urea appears to be the most satisfactory. Furthermore, the system

$$\text{urea phosphate} \rightleftharpoons \text{urea} + H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{\equiv}$$

assumes a pH in the presence of excess urea of such a value that the ideal is closely approximated. This buffer appears to have a wide concentration range of fairly constant acidity and also has a favorable tolerance to temperature variations. Similar conditions result in some of the other media discussed above, but urea appears to be the best. For example, substantial changes may be made in the treating solution containing urea without appreciably altering the solution pH or the cured cloth pH. How-

ever, when similar changes are made in a system involving gua
wide variations in pH occur, and if the guanidine is in excess the s
may become so decidedly basic that esterification is markedly re
and degradation accelerated.

However, it is advantageous to employ certain of the stronger n
bases in conjunction with an excess of a weaker buffering base. Th
system

$$\text{guanidine carbonate} \rightleftharpoons \text{guanidonium}^+ + HCO_3^- \rightleftharpoons OH^- + CO_2$$

is also buffered by excess urea at a pH slightly higher than that occ
in the absence of the guanidine carbonate. The mixed system seems
preferable from the standpoint of tolerances in reaction control an
rability of the products. Similar behavior is exhibited by dihyd
guanidine, guanylurea, aminoguanidine and biguanide. However,
these are all strong bases they are limited to use in the presence
excess of a buffer such as urea. When such mixed systems are use
resulting ester exists principally as the salt of the stronger base,
nitrogen to phosphorus ratios are increased. The complexity and sta
of these salts favors durability and the products are less suscepti
ion-exchange during leaching and laundering.

## b. Laboratory Impregnations

*Robert W. Little*

In the preceding section an attempt has been made to acquain
reader with the underlying principles governing the effectiveness and
manence of the urea-phosphate type of flameproofing treatment. Th
scription of actual laboratory investigations contained in the follo
pages serves to illustrate and substantiate the theoretical considera
It should be borne in mind that the fundamentals considered are eq
applicable regardless of the specific nature of the acid or amide emp
in any particular instance.

**Reaction Components.** Considering the simplest possible syste
mixture of urea and phosphoric acid, it may be well to review briefly
primary function of each of the components. As indicated in previous
tions, the flameproofing ingredient in these systems is the inorganic
or its ammonium salt. Ultimately the effects may be traced to the ac
acid anhydride itself. The amide or related compound included is inte
to serve in the capacity of a solvent for the reaction between the two
reactants and function in both the reduction of the tendering which acc
panies the reaction and the formation of simple or complex amido
which tend to increase the permanence of the treatment. The fla
resistant characteristics of the separate components are demonstrated
the data of Table 3. Obviously, urea by itself has no significant effect u

Table 3. Performance of the Separate Components of the Urea-Phosphate Treatment
*(Vertical-Bunsen Flame Test)*

| Material Added | Add-On % | Aftertreatment | Afterflame sec. | Afterglow sec. | Char Length in. |
|---|---|---|---|---|---|
| | | air dried | 25 | 110 | C.B.* |
| | | leached 30 min., tap water | 25 | 80 | C.B. |
| Urea | 14.6 | cured 15 min., 160° C | 27 | 91 | C.B. |
| | | cured and leached | 24 | 90 | C.B. |
| | | air dried | 0 | 0 | 3.7 |
| Phosphoric | 14.8 | leached 30 min., tap water | 25 | 5 | C.B. |
| Acid | | cured 15 min., 160° C | 0 | 1 | 3.5 |
| | | cured and leached | 14 | 0 | B.E.** |
| | | air dried | 0 | 0 | 3.2 |
| Urea: | | leached 30 min., tap water | 25 | 40 | C.B. |
| Phosphoric | 12.5 | cured 15 min., 160° C | 0 | 0 | 3.9 |
| Acid (1 : 1) | | cured and leached | 0 | 0 | 4.4 |

* C.B.—Completely burned.
** B E.—Burned to the end.

the resistance of the fabric to either afterflaming or afterglow. Orthophosphoric acid alone is an effective flameproofing agent but cannot be cured into the fabric to produce a permanent retardancy. An equal mixture of the two, on the other hand, imparts a high degree of flameproofness to the fabric which, when cured, is resistant to leaching.

The inclusion of additional components in the formula is intended to enhance the permanence of the retardancy and prevent, insofar as possible, the loss of fabric strength. The data presented in Table 4 show that the acidity of the impregnating solution is reduced practically to neutral by the addition of ammonium hydroxide. It is apparent, however, that the pH of the treating mixture is not the governing factor in the strength loss which occurs. The loss in strength with an initial solution pH of 1.5 is not appreciably greater than that occurring when the solution has a pH of 8 3. The deterioration of fabric strength is therefore closely associated with the actual reaction between cellulose and phosphoric acid. Apparently the majority of the loss in strength occurs within the first few minutes of the curing period. Continued curing beyond this point does not produce corresponding reduction in fabric strength but, as will be seen shortly, is essential in bringing about the salt formation and cross linkage required for permanence. The addition of formaldehyde does exert some protective action on the strength characteristics, which is due at least in part to the formation of a urea-formaldehyde resinous coating. Coincident with the gain in residual strength, however, is a reduction in the ability of the treated fabric to resist the ion-exchange tendencies of solutions containing alkali or alkaline earth ions. As seen in Figure 3, increasing the amount of formaldehyde in the impregnating bath appreciably reduced the re-

Table 4. Effect of the Addition of Ammonium Hydroxide and Formaldehyde in Preventing the Loss of Fabric Strength During the Cure

| Impregnating Solution | Urea + Phosphoric Acid Unheated | Urea + Phosphoric Acid Heated to 190° C. | Urea + Phosphoric Acid + Ammonium Hydroxide | Urea + Phosphoric Acid + Ammonium Hydroxide + Formaldehyde |
|---|---|---|---|---|
| pH | 1.5 | 6.0 | 8.3 | 7.6 |
| Add-On % | 16.0 | 17.5 | 17.5 | 12.0 |
| *Cure Time Min. at 150° C.* | *Warp Tensile Strength, lbs./in. (1-inch strip test)* | | | |
| 0 | 109 | 109 | 109 | 109 |
| 15 | 56 | 63 | 68 | 85 |
| 20 | 64 | 62 | 68 | 78 |
| 25 | 63 | 64 | 61 | 83 |
| 30 | 66 | 62 | 63 | 81 |

Table 6. Ion-Exchange Reactions of a Commercial Urea-Phosphate Type Fabric
(*45°-Microburner Flame Test*)

| | Flameproofness after 30 min. boil in leaching solution, followed by 15-min. cold water leach and drying | | | Flameproofness after boiling leached specimen in 5% ammonium chloride for 30 min., followed by 15-min. cold water leach and drying | | |
|---|---|---|---|---|---|---|
| Leaching Solution | Afterflame sec. | Afterglow sec. | Char Area in.² | Afterflame sec. | Afterglow sec. | Char Area in.² |
| None | 0 | 0 | 3.1 | — | — | — |
| Water | 0 | 0 | 3.3 | 0 | 0 | 3.7 |
| 5% Sodium chloride | 2 | 0 | 6.8 | 0 | 0 | 3.7 |
| 5% Calcium chloride | 60 | 0 | B.E.* | 0 | 0 | 4.5 |
| 5% Magnesium sulfate | 58 | 0 | B.E. | 0 | 0 | 5.5 |
| Synthetic sea water | 55 | 0 | B.E. | 0 | | |

sistance of the treated fabric to leaching in calcium chloride solutions. This might be attributed to a competition between the formaldehyde and phosphoric acid or cellulose phosphate ester for the urea available. The more of the amide that is tied up by the formaldehyde present, the less

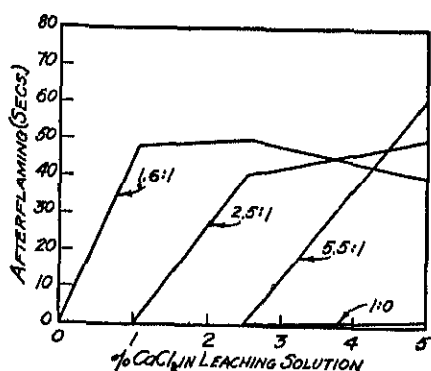



Figure 3. Effect of the addition of formaldehyde on the permanence of urea-phosphate treated fabrics. (The curves are for different ratios of urea: formaldehyde.)

is available for the formation of amido-type derivatives of the cellulose phosphate.

**Fabric Degradation.** Further evidence that the strength loss accompanying the flameproofing treatment is attributable to the combination of cellulose with the acid added is furnished by the data of Table 5. Exposure of untreated fabric to the same curing conditions produces no significant decrease in the tensile strength. In this case it is apparent that, although the majority of the tensile loss suffered occurs in the first two minutes of the curing period, prolonging the exposure progressively degrades the fabric though at a much slower rate.

Table 5. Effect of Time of Cure Upon the Tensile Strength of Fabric Treated with Urea-Phosphoric Acid

| | Cure Time Min. at 140° C. | Warp Tensile Strength lbs./in. (1-inch strip test) |
|---|---|---|
| Untreated | 0 | 113 |
| | 15 | 101 |
| | 30 | 107 |
| | 45 | 103 |
| | 60 | 112 |
| Treated | 2 | 76 |
| | 4 | 75 |
| | 6 | 72 |
| | 8 | 68 |
| | 10 | 61 |
| | 15 | 60 |

**Resistance to Ion-Exchange.** As emphasized in the preceding fundamental considerations, the ion-exchange phenomena are of vital importance with respect to this type of flameproofing process. This is readily

illustrated by a series of experiments of the type summarized in Table 6, showing the ease with which the amido salts of the cellulose-phosphate ester may be destroyed by leaching in high concentrations of sodium, calcium or magnesium ions. That the reaction involved is truly an ion-exchange is further substantiated by the recovery of flameproof characteristics when the ammonium salt of the ester is formed by leaching the impoverished fabric in a solution of ammonium chloride. The proof of the actual removal and re-addition of nitrogen is offered by the analytical data recorded in Table 7. The nitrogen content of the fabric is reduced

Table 7. Changes in Composition of a Commercial Urea-Phosphate Type Fabric Produced by Ion-Exchange Reactions

| Successive Treatments | Nitrogen Content % N | Phosphorous Content % $H_3PO_4$ | Molar Ratio N : $H_3PO_4$ |
|---|---|---|---|
| None | 2.23 | 8.97 | 1.78 |
| 30-min. boil in 5% calcium chloride, 15-min. cold water leach, dried 15 min. at 100° C. | 0.48 | 7.39 | 0.45 |
| 30-min. boil in 5% ammonium chloride, 15-min. cold water leach, dried 15 min. at 100° C. | 1.21 | 7.07 | 1.21 |

to practically one-fifth by the leaching in calcium chloride solution. Subsequent formation of the ammonium salt does not rebuild the nitrogen content to its former value but does replace sufficient nitrogen to raise the $N/H_3PO_4$ ratio above 1. The stability of the phosphate linkage to cellulose is demonstrated by the extent to which the phosphate content is retained throughout the leaching treatments. The resistance of the treated fabric to ionic transfers has been stated to be proportional to the amount of urea present in the impregnating solution and the extent to which it is converted to biuret, cyanuric acid and the melamines. Investigations of the influence of the urea:diammonium phosphate ratio in the solution upon the permanence of the resulting treatment illustrate this point. Fabric specimens impregnated with mixtures of these two materials in varying ratios were air-dried and then cured for 15 minutes at 150° C. For the sake of simplicity these treated fabrics are termed UDAP fabrics, employing a contraction of the components urea and diammonium phosphate. The results of this series of experiments are presented in Table 8 showing the relative strengths of the treated fabrics and their flameproofness after exposure to leaching conditions of varying severity. In this case, the strength of the fabric is only very slightly improved by incorporation of greater amounts of urea in the mixture. The effect upon the resistance to exchange with calcium ion is very apparent, however, and only with urea:phosphate ratios in the order of 4.4:1 molar, is the

Table 8. Effect of Increased Ratios of Urea : Diammonium Phosphate on the Resistance of UDAP Fabrics to Ion-Exchange
*(45°-Microburner Flame Test)*

| Molar Ratio Urea: Diammonium Phosphate | Warp Tensile Strength lbs./in. (strip)*** | Leaching Solution | After-flame sec. | After-glow sec. | Char Area in² |
|---|---|---|---|---|---|
| 0 : 1 | — | Cold water | 51 | 0 | C.B.* |
| 0.22 : 1 | 52 | Cold water | 46 | 0 | C.B. |
| | | Hot water | 72 | 0 | C.B. |
| 0.44 : 1 | 69 | Cold water | 0 | 0 | 4.6 |
| | | Hot water | 40 | 0 | B.E.** |
| 1.1 : 1 | 66 | Cold water | 0 | 0 | 2.4 |
| | | Hot water | 0 | 0 | 4.1 |
| | | 1% Calcium chloride | 34 | 0 | B.E. |
| | | 2.5% Calcium chloride | 57 | 0 | B.E. |
| | | 5.0% Calcium chloride | 63 | 7 | B.E. |
| 2.2 : 1 | 59 | Cold water | 0 | 0 | 2.4 |
| | | Hot water | 0 | 0 | 3.6 |
| | | 1% Calcium chloride | 0 | 0 | 4.8 |
| | | 2.5% Calcium chloride | 0 | 0 | 5.1 |
| | | 5.0% Calcium chloride | 33 | 0 | B.E. |
| 3.3 : 1 | 61 | Cold water | 0 | 0 | 2.2 |
| | | Hot water | 0 | 0 | 3.6 |
| | | 1% Calcium chloride | 0 | 0 | 3.9 |
| | | 2.5% Calcium chloride | 0 | 0 | 4.1 |
| | | 5.0% Calcium chloride | 3 | 0 | 3.9 |
| 4.4 : 1 | 62 | Cold water | 0 | 0 | 2.2 |
| | | Hot water | 0 | 0 | 2.3 |
| | | 1% Calcium chloride | 0 | 0 | 3.0 |
| | | 2.5% Calcium chloride | 0 | 0 | 3.5 |
| | | 5.0% Calcium chloride | 0 | 0 | 3.6 |

* C.B.—Completely burned.
** B.E.—Burned to the end.
*** Tensile strength of untreated fabric = 100–130 lbs./in.

treatment capable of resisting immersion in the 5% calcium chloride solution. With approximately a 1:1 molar ratio the fabric is just able to withstand a 30-minute immersion in boiling water. It is apparent, therefore, that in order to achieve permanent flameproofness it is not sufficient that there be only enough of the amide present to form a urea-phosphate salt but that an excess must be available to permit polymerization to cyanuric acid and melamine derivatives. Further reason for requiring an excess of urea is the loss which is incurred due to volatilization during the curing process.

**Effect of Other Acids and Amides.** According to fundamental considerations either of the components of the urea-phosphate system may

be replaced by materials of similar chemical nature. Substitutions of urea have been made using higher molecular weight amides such as dicyandiamide and the dicyanoguanidines. Similarly, orthophosphoric acid and its ammonium salts have been replaced by pyrophosphates, phosphamates and sulfamates. The theoretical considerations are similar in each case but the actual conditions required for effective treatment may vary widely. To serve as an illustration, data on a series of fabrics treated with urea-phosphate, urea-sulfamate, urea-sulfamate-phosphate and dicyandiamide phosphate have been assembled in Table 9. In each case the fabric speci-

Table 9. Effect of Replacement of Urea and Phosphate with Other Similar Compounds (*45°-Microburner Flame Test*)

| Treating Mixture % by Wt. | Solution Conc. % | Warp Tensile Strength lbs./in. (strip)*** | Successive Leaching Treatments | Add-On % | After-flame sec. | After-glow sec. | Char Area in² |
|---|---|---|---|---|---|---|---|
| Urea : | | | Cold water | 15.0 | 0 | 0 | 3.5 |
| Diammonium | | | Hot water | 11.6 | 0 | 0 | 3.8 |
| Phosphate | 46 | 63 | 30 min., sea water | — | 3 | 0 | 3.9 |
| (2 : 1) | | | 60 min., sea water | — | 3 | 0 | 5.2 |
| | | | 90 min., sea water | — | 28 | 0 | 6.8 |
| Urea : | | | Cold water | 9.8 | 0 | 0 | 2.5 |
| Ammonium | | | Hot water | 8.0 | 0 | 0 | 4.5 |
| Sulfamate : | 46 | 67 | 30 min., sea water | — | 43 | 250 | B.E.* |
| Diammonium | | | 60 min., sea water | — | 46 | 550 | B.E. |
| Phosphate | | | 90 min., sea water | — | 48 | 700 | B.E. |
| (20 : 7 : 3) | | | | | | | |
| Urea : | | | Cold water | 7.3 | 27 | 0 | B.E. |
| Ammonium | | | Hot water | 4.8 | 40 | 600 | B.E. |
| Sulfamate | 46 | 87 | 30 min., sea water | — | 63 | >300 | B.E. |
| (2 : 1) | | | 60 min., sea water | — | 58 | >300 | C.B.** |
| | | | 90 min., sea water | — | 63 | >300 | C.B. |
| Dicyandiamide: | | | Cold water | — | 0 | 0 | 2.8 |
| Diammonium | | | Hot water | — | 0 | 0 | 3.9 |
| Phosphate | 46 | — | 30 min., sea water | — | — | — | — |
| (2 : 1) | | | 60 min., sea water | — | — | — | — |
| | | | 90 min., sea water | — | — | — | — |
| Dicyandiamide: | | | Cold water | — | 0 | 0 | 3.0 |
| Diammonium | | | Hot water | — | 0 | 0 | 3.8 |
| Phosphate | 36.4 | 79 | 30 min., sea water | — | 65 | 0 | B.E. |
| (1 : 1) | | | 60 min., sea water | — | 68 | 0 | B.E. |
| | | | 90 min., sea water | — | 70 | 0 | B.E. |
| Dicyandiamide : | | | Cold water | — | 0 | 0 | 3.1 |
| Diammonium | | | Hot water | — | 0 | 0 | 3.4 |
| Phosphate | 30.8 | 83 | 30 min., sea water | — | 43 | 0 | B.E. |
| (1 : 2) | | | 60 min., sea water | — | 47 | 0 | B.E. |
| | | | 90 min., sea water | — | 43 | 0 | B.E. |

* B.E.—Burned to the end.
** C.B.—Completely burned.
*** Tensile strength of untreated fabric = 100–130 lbs./in.

mens were cured for 15 minutes at 140° C. These curing conditions are sub-optimum but serve in this instance to better illustrate the differences in permanence encountered. It is apparent that the substitution of ammonium sulfamate for the phosphate is advantageous in the prevention of tendering but that the retardant is not as readily cured into the fabric and as a result tends to produce low add-on fabrics possessing a much lower degree of permanence. The same is true of the mixture wherein dicyandiamide replaces urea in conjunction with diammonium phosphate. In order to achieve comparable effectiveness and permanence with these substitution mixtures it is necessary to increase the severity of the cure with respect to the time or temperature or both. This is further illustrated by the data of Table 10, comparing the effect of the time of cure upon the add-on and

Table 10. Effect of Time of Cure Upon the Permanence and Strength of Urea-Phosphate and Urea-Sulfamate Treated Fabrics — Sea Water Resistance
*(45°-Microburner Flame Test)*

| Treatment | Cure Time min. | Add-On % | Warp Tensile Strength lbs./in. (strip)*** | Time in Sea Water min. | After-flame sec. | After-glow sec. | Char Area in² |
|---|---|---|---|---|---|---|---|
| Urea : | 5 | 5.1 | 80.5 | 0 | 0 | 0 | 4.1 |
| Diammonium Phosphate; | | | | 60 | 50 | 45 | B.E.* |
| 2 : 1 by wt. | | | | 120 | 57 | 2 | B.E. |
| 46% solution | | | | | | | |
| Cured at 140° C. | 10 | 14.1 | 66.5 | 0 | 0 | 0 | 2.0 |
| | | | | 60 | 38 | 0 | B.E. |
| | | | | 120 | 39 | 0 | B.E. |
| | 15 | 15.6 | 68.5 | 0 | 0 | 0 | 2.5 |
| | | | | 60 | 2 | 0 | 2.8 |
| | | | | 120 | 0 | 0 | 2.9 |
| | 20 | 16.8 | 68.2 | 0 | 0 | 0 | 2.1 |
| | | | | 60 | 0 | 0 | 3.1 |
| | | | | 120 | 0 | 0 | 3.0 |
| | 25 | 18.0 | 62.7 | 0 | 0 | 0 | 2.2 |
| | | | | 60 | 0 | 0 | 2.9 |
| | | | | 120 | 0 | 0 | 2.7 |
| | 30 | 19.1 | 57.2 | 0 | 0 | 0 | 2.1 |
| | | | | 60 | 0 | 0 | 2.4 |
| | | | | 120 | 0 | 0 | 2.4 |
| | 40 | 20.5 | 57.5 | 0 | 0 | 0 | 2.2 |
| | | | | 60 | 0 | 0 | 2.6 |
| | | | | 120 | 0 | 0 | 2.4 |
| | 50 | 19.3 | 60.5 | 0 | 0 | 0 | 1.9 |
| | | | | 60 | 0 | 0 | 2.1 |
| | | | | 120 | 0 | 0 | 2.2 |
| | 60 | 19.4 | 60.5 | 0 | 0 | 0 | 2.2 |
| | | | | 60 | 0 | 0 | 2.2 |
| | | | | 120 | 0 | 0 | 2.0 |

*(Continued on next page)*

Table 10. Effect of Time of Cure Upon the Permanence and Strength of Urea-Phosphate and Urea-Sulfamate Treated Fabrics — Sea Water Resistance (*Continued*)
(*45°-Microburner Flame Test*)

| Treatment | Cure Time min. | Add-On % | Warp Tensile Strength lbs./in. (strip)*** | Time in Sea Water min. | After-flame sec. | After-glow sec. | Char Area in² |
|---|---|---|---|---|---|---|---|
| Urea : | 5 | 1.6 | 88 | 0 | 58 | 185 | C.B.** |
| Ammonium Sulfamate; | | | | 60 | 47 | >300 | C.B. |
| 2 : 1 by wt. | | | | 120 | 52 | 120 | C.B. |
| 46% solution | | | | | | | |
| Cured at 140° C. | 10 | 4.2 | 88 | 0 | 38 | 562 | B.E. |
| | | | | 60 | 73 | >300 | C.B. |
| | | | | 120 | 63 | >300 | C.B. |
| | 15 | 7.3 | 87 | 0 | 27 | 0 | B.E. |
| | | | | 60 | 58 | >300 | C.B. |
| | | | | 120 | 58 | >300 | C.B. |
| | 20 | 10.2 | 88 | 0 | 0 | 0 | 4.0 |
| | | | | 60 | 53 | 195 | B.E. |
| | | | | 120 | 48 | >300 | B.E. |
| | 25 | 9.9 | 88 | 0 | 0 | 0 | 4.5 |
| | | | | 60 | 48 | >300 | B.E. |
| | | | | 120 | 55 | >300 | C.B. |
| | 30 | 12.3 | 79 | 0 | 0 | 0 | 4.0 |
| | | | | 60 | 38 | >300 | B.E. |
| | | | | 120 | 38 | >300 | B.E. |
| | 40 | 15.8 | 81 | 0 | 0 | 0 | 3.1 |
| | | | | 60 | 5 | >300 | 4.5 |
| | | | | 120 | 2 | >300 | 4.8 |
| | 50 | 18.9 | 77 | 0 | 0 | 0 | 3.3 |
| | | | | 60 | 4 | >300 | 4.2 |
| | | | | 120 | 0 | >300 | 4.7 |
| | 60 | 23.5 | 74 | 0 | 0 | 0 | 3.0 |
| | | | | 60 | 3 | >300 | 4.6 |
| | | | | 120 | 0 | 152 | 4.3 |

* B.E.—Burned to the end.
** C.B.—Completely burned.
*** Tensile strength of untreated fabric = 100–130 lbs./in.

permanence obtained with the urea-phosphate and urea-sulfamate treatments. An effective and permanent treatment is obtained with the urea-phosphate system on curing for 20 minutes at 140° C. Additional curing beyond this point does not produce appreciable changes in the add-on, strength or flameproofness of the fabric. With urea-sulfamate, curing for 20 minutes at 140° C. again produces a fabric possessing good initial flameproofness and a residual fabric strength superior to the phosphate mixture. The add-on obtained is appreciably lower, however, and the effec-

tiveness of the retardancy is destroyed by immersion in synthetic ocean water. Increasing the time of cure in order to improve the resistance to ion-exchange, produces correspondingly higher add-ons but at the same time progressively reduces the strength of the treated fabric. Curing for as long as 60 minutes at 140° C. does not result in a permanence comparable to that obtained in the case of the phosphate with a 20-minute cure, in spite of the fact that the add-on is 50% greater. In other words, it is very probable that the production of a comparable fabric with the urea-sulfamate mixture by increasing the severity of the cure conditions would result in a fabric of appreciably higher add-on and very nearly the same tensile strength. It would appear therefore that variations in the con-

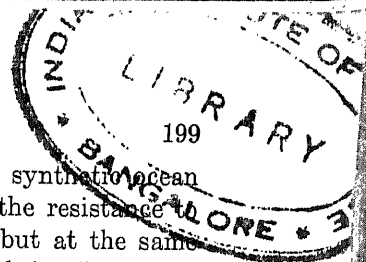
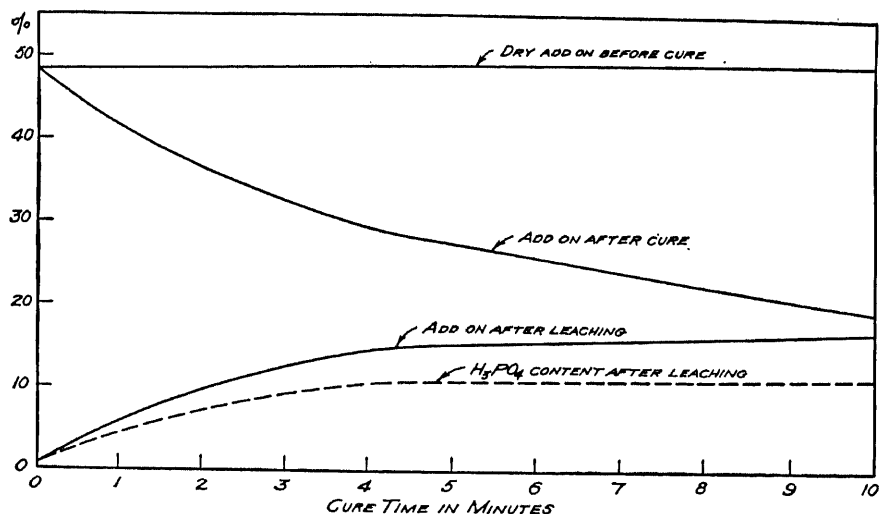



Figure 4. Fixation of urea-phosphate on curing (180° C.).

stituents employed in order to retain a maximum amount of strength in the treated fabric would produce a corresponding increase in the final add-on or decrease in the resistance of the processed fabric to ionic transfer. In view of the above and for the sake of simplicity the remaining considerations will be restricted to the simple system of urea and diammonium phosphate.

**Nitrogen to Phosphate Ratio.** The changes occurring in the amount of material added to the fabric and the composition of the mixture are illustrated by the data of Table 11 and the curves of Figure 4. Progressive curing is shown to produce a gradual sublimation of urea and fixation of phosphate in the fabric. Since the phosphate represents the primary flameproofing ingredient, it is apparent that in order to achieve an effective flameproofing treatment, the cure must be continued until the flat portion

Table 11. Variation of Phosphate Content and Permanence with Time and Temperature of Cure
*(45°-Microburner Flame Test)*

| Cure Temp. °C | Cure Time min. | Warp Tensile Strength lbs./in. (strip) | Add-On % Dried | Add-On % Cured | Add-On % Leached | % $H_3PO_4$ (Leached) | 30-Min. Water Leach After-flame sec. | 30-Min. Water Leach After-glow sec. | 30-Min. Water Leach Char Area in² | 2-Hr. Sea Water Leach After-flame sec. | 2-Hr. Sea Water Leach After-glow sec. | 2-Hr. Sea Water Leach Char Area in² |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| — | 0 | 103 | 48.6 | — | — | 11.8* | 0 | 0 | 2.4.* | — | — | — |
| — | 0 | 103 | 47.8 | — | 0.6 | 0.6 | 90 | 17 | B.E. | — | — | — |
| 160 | 2 | 104 | 43.1 | 39.7 | 0 | 0.5 | 104 | 0 | B.E. | 67 | 183 | B.E.** |
| | 4 | 86 | 46.9 | 37.1 | 9.9 | 6.0 | 0 | 0 | 2.9 | 56 | 0 | B.E. |
| | 6 | 81 | 51.0 | 34.7 | 13.9 | 8.8 | 0 | 0 | 2.9 | 48 | 0 | B.E. |
| | 8 | 79 | 52.2 | 32.4 | 18.6 | 8.4 | 0 | 1 | 3.0 | 0 | 0 | 2.7 |
| | 10 | 77 | 51.0 | 28.0 | 15.5 | 9.0 | 0 | 1 | 2.5 | 39 | 0 | B.E. |
| | 12 | 73 | 48.2 | 23.9 | 14.7 | 8.4 | 0 | 1 | 2.8 | 0 | 0 | 2.7 |
| | 14 | 69 | 48.3 | 23.9 | 13.6 | 9.3 | 0 | 0 | 2.1 | 0 | 0 | 2.7 |
| | 16 | 67 | 47.6 | 21.3 | 14.7 | 8.9 | 0 | 0 | 2.3 | 36 | 0 | B.E. |
| | 18 | 69 | 48.9 | 21.3 | 15.2 | 8.6 | 0 | 0 | 2.2 | 42 | 0 | B.E. |
| | 20 | 70 | 48.0 | 20.3 | 13.4 | 8.6 | 0 | 0 | 2.2 | 41 | 0 | B.E. |
| 170 | 2 | 98 | 49.8 | 43.3 | 3.1 | 2.9 | 49 | 0 | B.E. | 63 | 47 | B.E. |
| | 3 | 85 | 48.8 | 36.9 | 8.6 | 6.5 | 0 | 1 | 2.7 | 57 | 0 | B.E. |
| | 4 | 83 | 51.3 | 35.1 | 11.9 | 8.7 | 0 | 0 | 2.1 | 35 | 0 | B.E. |
| | 5 | 78 | 48.7 | 29.7 | 13.3 | 10.0 | 0 | 0 | 2.2 | 44 | 0 | B.E. |
| | 6 | 76 | 49.0 | 28.8 | 13.3 | 10.0 | 0 | 0 | 2.3 | 0 | 0 | 2.8 |
| | 7 | 74 | 48.4 | 26.2 | 14.1 | 10.5 | 0 | 0 | 2.2 | 34 | 0 | B.E. |
| | 9 | 73 | 48.7 | 23.3 | 14.5 | 11.1 | 0 | 0 | 2.4 | 36 | 0 | B.E. |
| | 11 | 71 | 49.7 | 21.8 | 16.7 | 10.4 | 0 | 0 | 2.3 | 33 | 0 | B.E. |
| | 13 | 66 | 49.1 | 20.9 | 16.5 | 8.9 | 0 | 0 | 2.5 | 0 | 0 | 2.7 |
| | 15 | 66 | 49.8 | 19.5 | 16.8 | 9.6 | 0 | 0 | 2.4 | 0 | 0 | 2.7 |

* —These specimens were not leached.
** B.E.—Burned to the end.

*(Continued on next page)*

Table 11. Variation of Phosphate Content and Permanence with Time and Temperature of Cure (*Continued*)
(*45°-Microburner Flame Test*)

| Cure Temp. °C. | Cure Time min. | Warp Tensile Strength lbs./in. (strip) | Add-On % | | | % $H_3PO_4$ (Leached) | 30-Min. Water Leach | | | 2-Hr. Sea Water Leach | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Dried | Cured | Leached | | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ |
| 180 | 2 | 85 | 47.1 | 38.7 | 8.2 | 4.9 | 0 | 1 | 3.7 | 46 | 0 | B.E.** |
| | 3 | 84 | 44.3 | 30.0 | 12.6 | 8.8 | 0 | 1 | 2.8 | 43 | 0 | B.E. |
| | 4 | 80 | 47.8 | 30.3 | 14.0 | 10.1 | 0 | 1 | 2.5 | 45 | 0 | B.E. |
| | 5 | 76 | 50.2 | 26.8 | 14.9 | 10.2 | 0 | 1 | 2.6 | 39 | 0 | B.E. |
| | 6 | 72 | 48.9 | 24.8 | 15.6 | 10.3 | 0 | 0 | 2.2 | 0 | 0 | 3.3 |
| | 7 | 72 | 48.9 | 23.0 | 15.1 | 9.9 | 0 | 0 | 2.8 | 2 | 0 | 3.1 |
| | 8 | 67 | 48.4 | 20.3 | 14.2 | 10.1 | 0 | 1 | 2.8 | 0 | 0 | 2.6 |
| | 9 | 66 | 49.5 | 19.8 | 15.4 | 9.9 | 0 | 1 | 2.9 | 0 | 0 | 2.8 |
| | 10 | 64 | 48.2 | 18.8 | 15.4 | 10.3 | 0 | 0 | 2.8 | 0 | 0 | 2.9 |

** B.E.—Burned to the end.

Table 12. Effect of Nitrogen Content and Nitrogen : Phosphoric Acid Ratio Upon the Permanence of Urea-Phosphate Treated Fabrics

| Add-On % | | | Analysis after 30-Min. Water Leach | | | Analysis after 2-Hr. Sea Water Leach | | | Flameproofness after Sea Water (45°-*Microburner Test*) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dry | Cured | Leached | % $H_3PO_4$ | % N | $\frac{N}{H_3PO_4}$ (molar) | % $H_3PO_4$ | % N | $\frac{N}{H_3PO_4}$ (molar) | After-flame sec. | After-glow sec. | Char Area in² |
| | | | *(Cured 30 min. at 140° C.)* | | | | | | | | |
| 57.0 | 34.0 | 17.3 | 11.1 | 2.2 | 1.4 | 5.4 | 0.49 | .58 | 0 | 0 | 2.3 |
| | | | | | | | | | 41 | 0 | B.E.* |
| 55.5 | 32.3 | 17.5 | 11.6 | 2.1 | 1.3 | 5.6 | 0.51 | .59 | 45 | 0 | B.E. |
| | | | | | | | | | 45 | 0 | B.E. |
| 54.5 | 27.4 | 17.7 | 12.1 | 2.3 | 1.3 | 6.4 | 0.66 | .69 | 0 | 0 | 2.5 |
| | | | | | | | | | 44 | 0 | B.E. |
| 53.7 | 33.6 | 16.8 | 11.4 | 2.3 | 1.4 | 6.1 | 0.54 | .63 | 0 | 0 | 2.2 |
| | | | | | | | | | 46 | 0 | B.E. |
| 55.0 | 33.4 | 15.2 | 11.2 | 2.6 | 1.6 | 6.2 | 0.51 | .57 | 43 | 0 | B.E. |
| | | | | | | | | | 49 | 0 | B.E. |
| 53.5 | 32.4 | 15.2 | 11.6 | 2.3 | 1.4 | 6.2 | 0.49 | .56 | 50 | 0 | B.E. |
| | | | | | | | | | 48 | 0 | B.E. |
| | | | *(Cured 15 min. at 180° C.)* | | | | | | | | |
| 47.2 | 20.0 | 15.9 | 11.5 | 2.3 | 1.4 | 8.1 | 1.0 | .85 | 38 | 0 | B.E. |
| | | | | | | | | | 0 | 1 | 2.5 |
| 47.0 | 19.6 | 15.9 | 10.6 | 2.2 | 1.4 | 8.5 | 0.9 | .77 | 0 | 2 | 2.5 |
| | | | | | | | | | 0 | 1 | 2.4 |
| 47.5 | 19.8 | 16.5 | 10.4 | 2.9 | 1.9 | 9.5 | 1.0 | .72 | 0 | 1 | 2.6 |
| | | | | | | | | | 0 | 0 | 2.8 |
| 48.2 | 20.3 | 16.3 | 11.1 | 2.6 | 1.6 | 9.2 | 0.9 | .71 | 0 | 0 | 2.5 |
| | | | | | | | | | 0 | 0 | 2.7 |
| 48.3 | 20.4 | 16.6 | 10.4 | 2.4 | 1.7 | 9.4 | 1.0 | .73 | 0 | 1 | 2.4 |
| | | | | | | | | | 0 | 1 | 2.6 |
| 46.6 | 19.9 | 16.6 | 11.7 | 2.4 | 1.4 | 9.2 | 0.9 | .68 | 38 | 0 | B.E. |
| | | | | | | | | | 39 | 0 | B.E. |
| | | | *(Cured 10 min. at 190° C.)* | | | | | | | | |
| 49.3 | 18.5 | 14.4 | 12.6 | 2.1 | 1.2 | 6.9 | 1.0 | 1.08 | 0 | 0 | 2.8 |
| | | | | | | | | | 0 | 0 | 2.5 |
| 49.0 | 18.0 | 14.2 | 9.5 | 2.1 | 1.6 | 6.9 | 1.0 | 1.08 | 0 | 0 | 2.8 |
| | | | | | | | | | 0 | 0 | 2.6 |
| 50.4 | 19.1 | 14.9 | 9.5 | 2.3 | 1.7 | 6.7 | 1.2 | 1.30 | 0 | 0 | 2.8 |
| | | | | | | | | | 0 | 0 | 2.5 |
| 49.7 | 18.1 | 14.5 | 9.5 | 2.3 | 1.7 | 6.3 | 1.0 | 1.11 | 0 | 0 | 2.8 |
| | | | | | | | | | 0 | 0 | 2.5 |
| 49.3 | 16.6 | 14.4 | 12.0 | 2.3 | 1.3 | 6.8 | 1.1 | 1.12 | 0 | 0 | 2.6 |
| | | | | | | | | | 0 | 0 | 2.6 |
| 49.1 | 16.7 | 14.5 | 12.2 | 2.4 | 1.4 | 6.2 | 1.0 | 1.12 | 0 | 0 | 2.7 |
| | | | | | | | | | 0 | 0 | 2.5 |

* B.E.—Burned to the end.

of the add-on or phosphate content curves have been reached, or until a maximum fixation of phosphate has been accomplished. As shown by the flame test data of Table 11, however, this insures an adequate initial flameproofness but does not guarantee a permanent retardancy. The phosphate content alone does not represent the governing factor in the resistance of the fabric to leaching action. Many of the fabrics showing poor resistance to ion exchange contain the required amount of phosphate, which appears to be in the order of 9 to 10%. As previously discussed, the permanence of the treatment is more dependent upon the degree of salt formation and the extent of the polymerization and cross linkage of the amide. The permanent flameproofness, therefore, should be proportional, not to the phosphate content, but rather to the nitrogen to phosphate ratio. This is well illustrated by the data presented in Table 12. When the cure is insufficient to produce the required fixation of the nitrogen-bearing component, the sea water leach results in appreciable loss of nitrogen and the $N/H_3PO_4$ ratio is reduced from approximately 1.4 to the order of 0.63. In the majority of cases these treated fabrics lose their flame-resistant characteristics at the same time. With an adequate cure, on the other hand, the $N/H_3PO_4$ ratio is reduced only slightly in the course of the leaching treatment. In these cases, where the residual $N/H_3PO_4$ ratio remains above 1, the fabrics retain their flame-resistant properties even though the add-on is appreciably lower. These data clearly indicate that the permanence attained is practically unrelated to the phosphate content once the minimum requirement of 6–7% has been satisfied.

**Uniformity of Treatment.** It has been postulated in the past that the added phosphate tends to concentrate preferentially in the yarns of lower twist. This would lead to a preponderance of phosphate in the filling threads. In an attempt to substantiate or repudiate these claims, a series of treated fabrics were tested as to the phosphate content of the warp and fill threads. The analytical data of Table 13 indicate that no such preferential fixation occurs, the phosphate being uniformly distributed throughout the fabric. In some cases the use of heavily sized fabrics did make it difficult to obtain a uniform distribution of the flameproofing mixture. This, too, would tend to produce a higher phosphate concentration in the filling threads since the warp is generally more heavily sized. This could not be completely obviated even by the use of effective wetting agents. It is preferable, therefore, with this type of flameproofing treatment, which is so greatly dependent upon adequate penetration of the fabric, to use cloth which has been rendered highly absorbent by a preliminary desizing treatment.

**Optimum Curing Conditions.** In an attempt to fix the variables of the curing process in the urea-diammonium phosphate flameproofing system, an extended series of experiments were conducted in which a great

Table 13. Distribution of Phosphate in the Warp and Filling Threads of Treated Fabric*

| Cure Time min. | Weight Ratio warp/filling | % $H_3PO_4$ warp | % $H_3PO_4$ filling | $H_3PO_4$ Ratio warp/fill (by weight) | $H_3PO_4$ Ratio warp/fill (by area) |
|---|---|---|---|---|---|
| 2 | 1.42 | 3.6 | 3.3 | 1.09 | 1.55 |
| | 1.32 | 3.4 | 2.6 | 1.30 | 1.72 |
| 3 | 1.28 | 7.5 | 8.2 | 0.92 | 1.17 |
| | 1.28 | 7.1 | 6.8 | 1.04 | 1.33 |
| 4 | 1.34 | 7.7 | 7.5 | 1.02 | 1.37 |
| | 1.38 | 8.4 | 7.7 | 1.09 | 1.50 |
| 5 | 1.35 | 8.8 | 8.6 | 1.02 | 1.38 |
| | 1.38 | 9.4 | 5.7 | 1.65 | 2.28 |
| 6 | 1.46 | 9.5 | 8.8 | 1.07 | 1.57 |
| | 1.37 | 9.5 | 9.3 | 1.02 | 1.40 |
| 7 | 1.31 | 8.7 | 8.5 | 1.02 | 1.34 |
| | 1.28 | 8.7 | 8.4 | 1.03 | 1.32 |
| 8 | 1.36 | 10.0 | 7.8 | 1.28 | 1.74 |
| | 1.29 | 10.0 | 8.6 | 1.16 | 1.50 |
| 9 | 1.33 | 10.0 | 8.9 | 1.12 | 1.49 |
| | 1.35 | 9.7 | 8.1 | 1.20 | 1.62 |
| 10 | 1.31 | 10.8 | 10.1 | 1.07 | 1.40 |
| | 1.40 | 10.3 | 9.5 | 1.10 | 1.52 |

* Regular 8.5 oz. herringbone twill treated with a 46% solution of urea: diammonium phosphate (4.4 : 1 molar) containing 0.15% turkey red oil; cured at 180° C. and leached for 30 minutes in cold water.

many specimens of herringbone twill were cured at various temperatures for different lengths of time and studies made of the resistance of the fabric to sea water leaching and laundering and the tensile strength of the treated fabric. The number of specimens employed for any one set of curing conditions varied from 5 to 30, depending upon the consistency of the results obtained. In essence, the treating process consisted of immersing in a 46% solution containing urea and diammonium phosphate in the ratio of 2 to 1 by weight, or 4.4 to 1 molar. The fabric was then squeezed to a wet pickup of approximately 100%, air-dried, cured, washed in hot and cold water and finally air-dried. The effect of cure time and temperature upon the resistance of the treated fabric to the sea water leaching test is summarized in Table 14. It was possible as a result of these investigations to determine the minimum times of cure required at each curing temperature. In Table 15 a similar set of data are presented for the resistance of the treated fabric to laundering in 0.5% G.I. soap. Comparison of the two series will indicate that the sea water leaching test is a more severe criterion of the permanence of the treatment than six laun-

Table 14. Effect of Cure Time and Cure Temperature Upon the Resistance of UDAP Fabric to a 2-Hr. Leach in Sea Water

*(45°-Microburner Test)*

| Cure Temp. °C. | Cure Time min. | Add-On % | Afterflame sec. | Afterglow sec. | Char Area in² |
|---|---|---|---|---|---|
| 150 | 10 | — | 39 | 0 | B.E.** |
| | 15 | — | 17 | 0 | 3.2 |
| | 16 | 17.0 | 0 | 0 | 3.2 |
| | 18 | 16.9 | 19 | 0 | 3.5 |
| | 20 | 16.7 | 0 | 0 | 2.8 |
| | 22 | 13.9* | 19 | 0 | 3.5 |
| | 24 | 13.7* | 44 | 0 | B.E. |
| | 25 | 15.9 | 0 | 0 | 2.6 |
| 160 | 11 | 16.7 | 19 | 0 | 3.3 |
| | 13 | 16.7 | 0 | 0 | 3.0 |
| | 15 | 15.5 | 0 | 0 | 3.2 |
| | 20 | 16.1 | 0 | 0 | 3.2 |
| | 25 | 15.9 | 0 | 0 | 3.0 |
| 170 | 8 | 16.7 | 0 | 0 | 3.1 |
| | 10 | 16.6 | 0 | 0 | 2.7 |
| | 12 | 16.2 | 0 | 0 | 2.8 |
| | 15 | — | 0 | 0 | 2.4 |
| 180 | 4 | 12.7 | 42 | 0 | B.E. |
| | 6 | 16.7 | 14 | 0 | 3.1 |
| | 8 | 15.6 | 23 | 0 | 3.3 |
| | 10 | 16.6 | 14 | 0 | 3.2 |
| | 12 | 16.4 | 0 | 0 | 2.5 |
| | 15 | 15.8 | 0 | 0 | 2.8 |
| 190 | 4 | 16.1 | 15 | 0 | 3.4 |
| | 6 | 17.3 | 0 | 0 | 2.7 |
| | 8 | 16.9 | 0 | 0 | 2.7 |
| | 10 | 16.4 | 0 | 0 | 2.5 |
| | 12 | 15.1 | 0 | 0 | 2.9 |
| 200 | 1 | 1.5 | 53 | 60 | B.E. |
| | 2 | 3.4 | 46 | 0 | B.E. |
| | 3 | 15.6 | 1 | 0 | 2.6 |
| | 4 | 14.0 | 43 | 0 | B.E. |
| | 5 | 17.0 | 0 | 0 | 3.0 |
| | 6 | 15.7 | 0 | 0 | 3.0 |

* Insufficient add-on for permanent flameproofing.
** B.E.—Burned to the end.

derings in G.I. soap. In either case it is apparent that the permanence of the treatment shows the customary improvement with an increase in either the time or temperature of cure. The corresponding variation in the residual strength of the fabric is shown in Table 16. As previously indicated, working at odds with the permanence obtained, the strength is progres-

Table 15. Effect of Cure Time and Cure Temperature Upon the Resistance of UDAP Fabric to Laundering in G.I. Soap

*(45°-Microburner Test)*

| Cure Temp. °C. | Cure Time min. | No. of Launderings | Afterflame sec. | Afterglow sec. | Char Area in² |
|---|---|---|---|---|---|
| 140 | 20 | 1 | 0 | 0 | 2.4 |
| | | 3 | 0 | 0 | 2.3 |
| | | 6 | 44 | 0 | B.E.* |
| | 30 | 1 | 0 | 0 | 2.4 |
| | | 3 | 0 | 0 | 2.3 |
| | | 6 | 41 | 0 | B.E. |
| | 40 | 1 | 0 | 0 | 2.5 |
| | | 3 | 0 | 0 | 2.4 |
| | | 6 | 0 | 0 | 2.1 |
| 160 | 15 | 1 | 0 | 2 | 2.7 |
| | | 3 | 0 | 0 | 2.9 |
| | | 6 | 0 | 0 | 2.6 |
| | 20 | 1 | 0 | 0 | 2.6 |
| | | 3 | 0 | 0 | 2.8 |
| | | 6 | 0 | 0 | 2.6 |
| | 25 | 1 | 0 | 0 | 2.6 |
| | | 3 | 0 | 0 | 3.0 |
| | | 6 | 0 | 0 | 2.5 |
| 180 | 10 | 1 | 0 | 2 | 2.6 |
| | | 3 | 0 | 0 | 2.3 |
| | | 6 | 0 | 2 | 2.1 |
| | 12 | 1 | 0 | 0 | 2.6 |
| | | 3 | 0 | 0 | 2.5 |
| | | 6 | 0 | 2 | 2.3 |
| | 14 | 1 | 0 | 2 | 2.6 |
| | | 3 | 0 | 0 | 2.6 |
| | | 6 | 0 | 2 | 2.2 |
| 190 | 4 | 1 | 0 | 0 | 2.5 |
| | | 3 | 0 | 0 | 2.4 |
| | | 6 | 0 | 0 | 1.9 |
| | 6 | 1 | 0 | 2 | 2.7 |
| | | 3 | 0 | 0 | 2.3 |
| | | 6 | 0 | 2 | 2.1 |
| | 8 | 1 | 0 | 0 | 2.6 |
| | | 3 | 0 | 0 | 2.3 |
| | | 6 | 0 | 3 | 2.1 |
| 200 | 4 | 1 | 0 | 0 | 2.6 |
| | | 3 | 0 | 2 | 2.3 |
| | | 6 | 0 | 4 | 1.9 |
| | 5 | 1 | 0 | 2 | 2.7 |
| | | 3 | 0 | 2 | 2.2 |
| | | 6 | 0 | 3 | 2.1 |
| | 6 | 1 | 0 | 0 | 2.7 |
| | | 3 | 0 | 2 | 2.3 |
| | | 6 | 0 | 3 | 1.9 |

* B.E.—Burned to the end.

Table 16. Variation of Fabric Strength with Time and Temperature of Cure
*(1-inch Raveled Strip Test)*

| Cure Temp. °C. | Cure Time min. | Warp Tensile Strength * lbs./in. |
|---|---|---|
| Untreated 8.5 oz. Herringbone Twill | | 131 |
| 140 | 20 | 83 |
| | 30 | 78 |
| | 40 | 77 |
| 150 | 10 | 75 |
| | 15 | 70 |
| | 16 | 72 |
| | 18 | 73 |
| | 20 | 74 |
| | 22 | 74 |
| | 24 | 75 |
| 160 | 11 | 73 |
| | 13 | 70 |
| | 15 | 71 |
| | 20 | 67 |
| | 25 | 64 |
| 170 | 8 | 69 |
| | 10 | 66 |
| | 12 | 65 |
| 180 | 4 | 85 |
| | 6 | 69 |
| | 8 | 63 |
| | 10 | 61 |
| | 12 | 58 |
| | 14 | 54 |
| 190 | 4 | 71 |
| | 6 | 67 |
| | 8 | 55 |
| | 10 | 50 |
| | 12 | 50 |
| 200 | 1 | 100 |
| | 2 | 82 |
| | 3 | 74 |
| | 4 | 66 |
| | 5 | 59 |
| | 6 | 50 |

* Average of ten specimens.

sively degraded by increasing the intensity or duration of the curing period, though the majority of the loss occurs in the first few minutes of curing in all cases.

It is obvious that in order to obtain the best possible fabric by this process, it is necessary to compromise the permanence with the loss of

strength suffered. Setting the resistance to 2 hours' immersion in sea water as the primary requirement, the optimum conditions for the treatment are represented diagrammatically in Figure 5. Since it is also desirable to retain the maximum amount of fabric strength and, at the same time, keep the curing time sufficiently short to be commercially practical, the preferable curing conditions for this treatment were selected as 13 minutes' cure at 160° C.

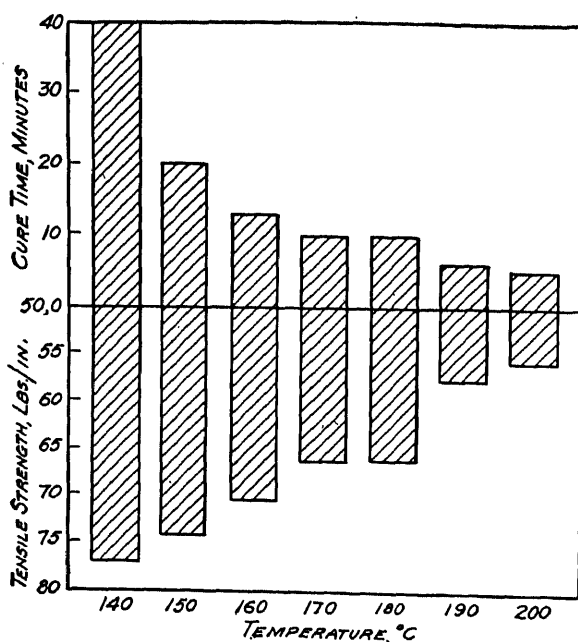



Figure 5. Optimum curing conditions for the UDAP Process.

In order to compare the performance of a flameproofed fabric treated according to the above process with that of the other available durably treated fabrics, a small-scale mill run was carried out. The exact conditions specified could not be attained on the available equipment, but the process was essentially as follows:

*Impregnating Bath*

| | |
|---|---|
| Urea | 300 lbs. |
| Diammonium phosphate | 150 lbs. |
| Tergitol | 1 lb. |
| Water | 339 lbs. (41 gals.) |
| Total volume | 80 gals. |
| Concentration | 56% |
| Approximate pH | 8.0 |

The squeeze rolls were adjusted for an 80% wet pickup, producing a wet add-on of 45% from the 56% solution. This is comparable to the desired 100% pickup from a 46% solution. The cure was carried out for 7 minutes, 10 seconds at 174.4° C., which was somewhat less than the optimum combination desired. The treated fabric was finally washed in hot and cold water, dried and subjected to standard finishing processes.

Comparisons of this treated fabric with several other durably flameproofed materials are described in the following chapter, with respect to the performance characteristics of the fabric itself as well as the physical and physiological influences which might be exerted upon the wearer of a flameproofed garment. Identical evaluation data are also presented for a commercially developed fabric processed with a similar but perhaps more complex flameproofing mixture.

The variables existent and problems encountered in the commercial application of this type of flameproofing treatment are considered in the following section.

## c. Industrial Processing

*William P. Hall*

Extensive development has been carried out on the commercial application of the modified cellulose method of imparting flame-resistance * and substantial quantities of commercially treated materials have been produced.

As far as textiles are concerned the processes developed may be applied with equal success to loose fibers, yarns or fabrics. This discussion, however, will deal only with the commercial application to cotton fabrics, although the processes may also be applied to cellulose rayon and protein fabrics.

### *(1) Fabric Preparation*

Since this method of flameproofing involves a reaction with the cellulose it is beneficial to have the fabric in the pure form, that is, sizing and natural waxes and other impurities should be removed. This is usually accomplished by desizing with enzymes and scouring with detergents and caustic soda followed by washing and bleaching. The reactivity of the flame-retardant chemicals toward the cellulose may be further increased by mercerizing the fabric completely. This treatment primarily increases the durability of the finish to washing and leaching.

* Various aspects of the developments described are covered by patent applications of Joseph Bancroft and Sons Co., Wilmington, Del.

In case the fabric is to be dyed or printed it is desirable to apply such processes prior to the application of the flameproofing treatment. This is recommended for several reasons: first, to obtain uniform dyeings it is essential to distribute the dyestuff uniformly upon the fibers, and this is not possible after the finish has been applied; second, the application of dyestuffs of good durability such as vats, naphthols, and pigments involves the use of strong chemical solutions having a detrimental effect upon the flame-resistant finish.

It is therefore evident that printing and dyeing should be done prior to flameproofing and should preferably involve the use of vat and naphthol dyes to obtain maximum color durability. The application of the finish may produce a slight change in shade, this change being dependent primarily upon the type of dyestuff used. In general, however, the change is insignificant and a suitable range of shades may be obtained without difficulty. The use of mineral dyeings is possible but not recommended since the deposition of large quantities of metallic oxides and salts in the fabric may produce an undesirable "afterglow" condition.

The dyeing with pigment mixtures containing plastic and resinous binders is possible but not recommended, especially if the pigments are of a mineral character in which case an "afterglow" condition may be produced in the finished fabric. Besides, the binders used, if they are combustible in nature, may undesirably interfere with the flame-retardant properties.

A pure mercerized dyed fabric of good absorbency gives the best all-around results. Pretreatment with sizing materials may be practiced provided such materials do not detrimentally interfere with the successful applications of the process. If protein or carbohydrate sizing materials are used the flame-retardant chemicals will react with these materials as well as with the cellulose of the fabric. However, the use of large quantities of such presizing materials is not desirable since the stiffness and absorbency of the fabric will be undesirably altered.

### (2) *Preparation of Flameproofing Solution*

As shown in the two preceding sections of this chapter, the composition of the flameproofing mixture may be varied by altering the chemical ingredients or by altering the method of preparing the mixture.

The main ingredients may be divided into two classes, namely, the acids and the nitrogen compounds. These may vary as previously shown between wide limits, but each is essential to the successful application of the process.

For the same ingredients different results may be obtained by varying the method of preparing the mixture. For example, one or several of the ingredients may be fused at high temperatures and then added to the

mixture, or the ingredients may be divided into different sections and these reacted together followed by a mixing of the different sections to produce the final impregnating mixture.

Acids of phosphorus, such as orthophosphoric and pyrophosphoric, are usually employed as well as the more complex amido phosphoric and phosphonitride acids. Many nitrogen compounds, principally those containing a high percentage of nitrogen such as urea, guanidine, dicyandiamide, melamine and biuret, also find wide use.

A suitable mixture may be prepared by mixing in the cold 1000 lbs. diammonium phosphate, 2000 lbs. urea and 3000 lbs. water. Another mixture is prepared by mixing together 215 lbs. orthophosphoric acid (75%), 3000 lbs. urea, 160 lbs. guanidine carbonate and enough water to make 100 gallons. Another mixture is prepared by reacting together at high temperatures 200 lbs. of orthophosphoric acid (75%) and 400 lbs. of urea; after cooling the following are added: 28 lbs. mill ammonia, 108 lbs. formaldehyde (37%), and enough water to make 100 gallons.

Other auxiliary ingredients may be added to the mixture such as penetrating agents, waterproofing agents, softeners and the like. In general, the use of these materials in the mixture is not recommended.

The mixing equipment used in preparing the flameproofing mixture consists of a stainless steel tank, hooded to remove fumes, and equipped with a slow speed agitator and with suitable means of heating and cooling. The heating may be done by steam, electricity or gas and the cooling with cold brine or water. A jacketed steel tank using steam and cold water for heating and cooling is generally satisfactory. Also in the case where very rapid cooling is desired, water will not be satisfactory and supercooled brine should be employed.

To measure and control the temperature of the mix, a thermometer or similar instrument should be inserted in the lower portion of the tank. Also, since the quantity of mixture prepared in commercial practice is usually determined by the final volume rather than weight, it is desirable to install a float type volume indicator so that the volume can be easily measured.

Two mixing tanks should be available to insure a steady supply of solution, or one mixing tank and one jacketed or insulated storage tank may be used. The storage tanks or mixing tanks should feed directly to the solution application equipment, the steel or iron feed pipes being insulated to prevent excessive cooling of the mixture in passing from the tanks to the impregnating bath (see Figure 10).

Since the flameproofing of fabrics involves the use of concentrated chemical solutions the quantity of chemicals used becomes very large as compared with other textile processes. It is therefore necessary to insure sufficient storage space and the necessary mechanical equipment for the handling of such large quantities of chemicals. For example, processing

10,000 yards of fabric weighing 8 oz./yd. may require 1700 lbs. of diammonium phosphate and 2400 lbs. of urea.

### *(3) Treating Process*

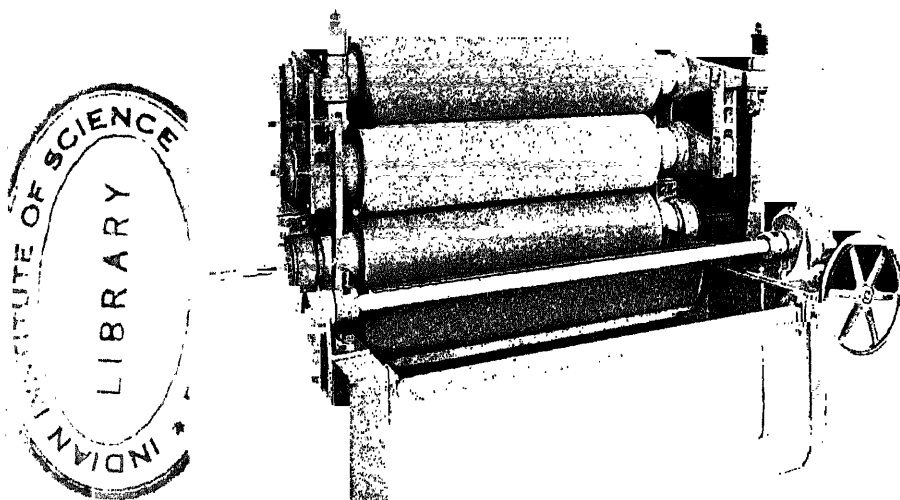
The flameproofing solution may be applied by any of the methods well known in the textile industry. However, the most common procedure is to impregnate the fabric with the solution and remove the excess by squeezing. This procedure is referred to as "mangling" or "padding" and the equipment as a mangle or padder. A two-roll mangle containing a jacketed stainless steel box with sufficient dips to insure a thorough impregnation of the fabric generally serves very well, but a three-roll double dip mangle with a jacketed stainless steel dip box is recommended since this method of application insures a uniform and efficient penetration of the fabric.

*Courtesy of H. W. Butterworth & Sons Company, Philadelphia, Pa.*

Figure 6. Three-roll micro-set mangle.

The jacket on the bath should be steam or hot water heated to insure temperature control of the solution which in most cases, due to the high solid content, is applied at elevated temperature to prevent undesirable crystallization at lower temperatures. To control the temperature a thermometer or similar instrument should be inserted in a suitable place in the bath. The type of squeeze roll used in the mangle may be of steel, wood, husk or rubber. Brass is not recommended due to the presence of ammonia in some of the flameproofing solutions. For the same reason brass rollers should not be used in the bath.

The squeezing mechanism should be capable of applying a uniform squeeze from selvage to selvage at both high and low pressures. Mangles where the pressure is applied by weights or hand set screws are satisfactory but a pneumatic pressure mangle with individual cylinder pressure adjustment is highly recommended since the uniformity can be easily controlled and duplicated from run to run.

The wet pickup and the solution concentration determine the quantity of chemicals deposited on the fabric. For a particular solution the squeeze on the cloth is therefore adjusted to obtain the desired quantity of chemicals on the fabric. By wet pickup is meant the difference in weight between the fabric before and after impregnation. For most applications 75% to 100% pickup is satisfactory.

After applying the solution, the cloth may be dried directly or it may be left in the moist condition for a short time. To increase speed of production and decrease labor cost the impregnating mangle is usually placed in front of the drying unit and the cloth passes directly from the impregnation to the drying without being folded or batched.

### (4) *Drying*

Since the quantity of solid material deposited on the cloth is usually high, the quantity of water to be removed is not excessive. It usually averages about 50% of the solution deposited. Such drying equipment as hot cans, flue dryers, air-lay dryers, frame dryers, or loop dryers may be used successfully. The most satisfactory method of drying is obtained with a tenter frame where the cloth is held by clips and tightly stretched while drying, thus affording control of the width of the cloth. This width control is sometimes very important and cannot be obtained with the other types of drying equipment. Due to the stiffness of the dried fabric, especially the heavy variety, the loop and air-lay type of equipment is the least recommendable since the formation of loops and folds at this stage of the process may permanently injure the cloth.

Since the cloth usually carries a heavy quantity of chemicals it is advantageous while the moisture content is still high to prevent the cloth from passing over stationary objects such as bars or rails as the flame-retardant mixture will be scraped off, resulting in an unnecessary loss of chemicals. This may be prevented by passing the cloth over freely rotating rollers, or passing it through a preliminary flue dryer where the excess moisture may be removed quickly while the cloth is freely suspended. Infrared heating equipment such as infrared lamps may also be used for this purpose.

The cloth is usually quite hot and shows an acid reaction on the completion of the drying operation. This is quite an undesirable state and to prevent excessive detrimental action to the fabric it is usually passed

directly through a cooling chamber or over cooling cans before being batched into rolls (see Figure 10).

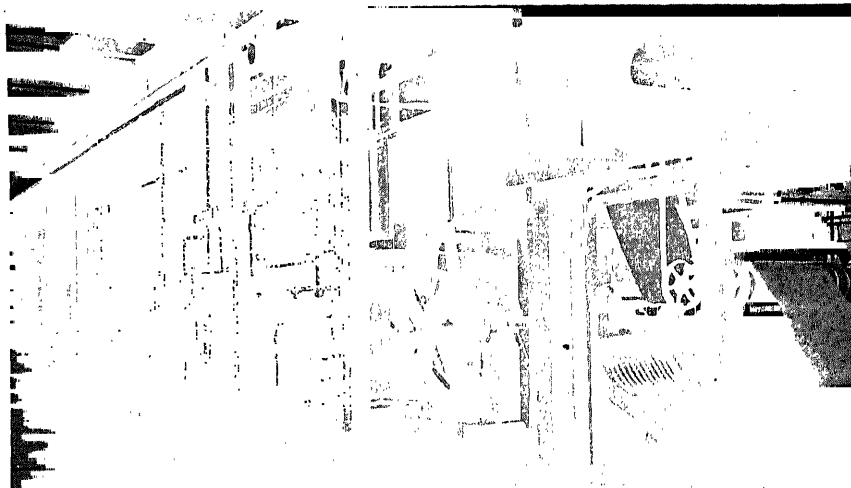
The cloth after drying and cooling is quite stiff and care should be taken to prevent the formation of creases and folds as this may permanently injure the fabric. It is therefore evident that the cloth should always be

*Courtesy of Joseph Bancroft & Sons Company, Wilmington, Del.*

Figure 7. Commercial impregnation and drying installation showing a continuous range consisting of a mangle, overhead flue dryer and tenter frame.

wound into rolls after drying rather than folded into boxes as is often the practice in regular textile processing.

### (5) *Curing*

The curing or aging of the impregnated and dried fabric represents one of the most important steps in the process. As previously described, it is during the curing that the combination between the cellulose of the fabric and the acid phosphates of the solution takes place. In many cases additional changes also take place in the chemical ingredients themselves during this curing operation.

The curing is controlled by varying the time and temperature and is determined primarily by the composition of the impregnating mixture, type of fabric and the degree of durability desired. Excessive time of curing or very high temperatures cause undesirable changes in the physical properties of the fabric, especially in the tensile and tearing strength, although under such conditions the durability of the finish is substantially increased. It is therefore necessary to determine and control carefully the curing conditions for a particular run in order to obtain the most satisfactory all-around results.

For all practical purposes a temperature range of from 300° F. to 350° F. is satisfactory with the time varying from 15 minutes to 3 minutes. As an average, using medium and heavy weight cotton fabrics, a time of 7 minutes and a temperature of 335° F. give good results.

The temperature range of curing is obtainable with standard textile drying and curing equipment but the time of curing is excessively long for regular equipment. A loop or air-lay type of dryer would be satisfactory as far as time and temperature are concerned but these machines are not well adapted to this part of the process as will be presently shown.

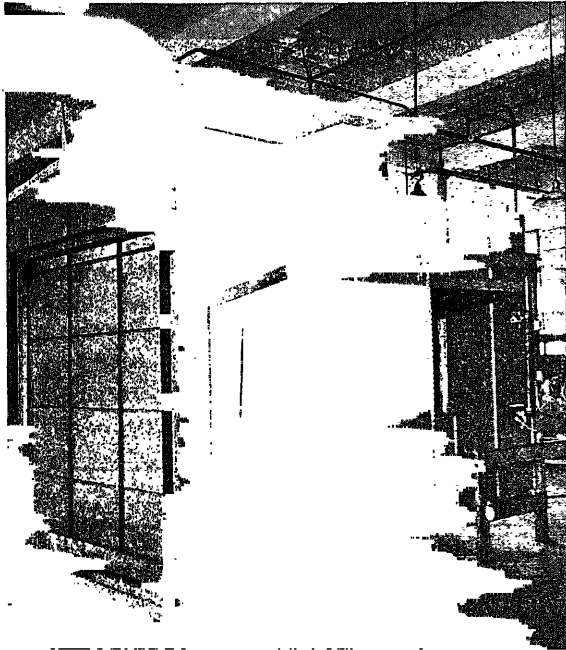
Ordinary type drying and curing equipment not of the loop and slack

*Courtesy of Andrews and Goodrich, Inc., Boston, Mass.*

Figure 8. Gas-heated curing oven.

type such as drying frames, super-heated drying cans, flue dryers, and resin curing chambers may be used with success. However, the output of these machines would be small using material which required a 7-minute cure time. The construction of super-heated cans of sufficient number or a frame of sufficient length to insure proper curing and a satisfactory output would be impractical and uneconomical. This leaves the flue type dryer or curing chamber as the only suitable equipment which will produce the proper conditions of time and temperature and at the same time assure a satisfactory practical commercial output.

Generally, this type of equipment consists of one small preheating

chamber followed by a larger baking chamber. The cloth is carried in open width over a series of rollers while hot air is being circulated around the cloth. In the preheating section the heated air is blown through slots directly onto the cloth in order to bring it quickly to the desired temperature, while in the baking section the cloth is maintained at this temperature for the desired length of time.

To maintain the temperature in the curing chamber at the desired value, the air is circulated by fans through an indirect heat exchange unit where the heat may be supplied by steam, gas or oil. The direct heating of the circulating air by gas or oil burners is also practiced. The curing of the fabric by infrared lamps or by electronic means is not practical and is uneconomical.

The cloth while in the ager is kept in open width and passes under tension over a series of rollers at the top and bottom of the curing chamber; this prevents the formation of sharp creases which would seriously and permanently injure the fabric. The necessity of keeping the fabric from folding and creasing makes the use of loop and air-lay type of curing equipment unsuitable except for very light fabrics where the stiffness and weight would be small.

The size of the curing equipment, that is, the length of cloth in the machine at one time, together with the length of curing time determines the production capacity of a given piece of equipment. For a given curing time of 6 minutes, for example, and with 120 yards of cloth capacity a production rate of 20 yards a minute may be obtained.

The cloth is slightly acidic upon completion of curing and it is best that the fabric be cooled before being batched into rolls. This procedure will prevent any unnecessary degradation in case it is necessary to store the cloth for a substantial length of time before washing.

### *(6) Washing and Drying*

The cloth after curing contains a large quantity of soluble material which it is desirable to remove in order to reduce the stiffness and return the fabric more nearly to its original hand and feel. To avoid the formation of creases at this stage it is recommended that open width washing equipment be employed such as jigs, open width soapers and vertical or horizontal multiroll washers.

In jig washing operations the cloth is passed back and forth under tension through a water bath until the soluble chemicals are removed and is finally squeezed or extracted to remove the excess water.

In the open width soaper the cloth passes under tension through a series of multi-dip wash boxes containing hot water, the excess water being removed by squeezing after each box. Any number of wash boxes may be employed but two to four boxes are sufficient for most fabrics.

In the vertical or horizontal multiroll washers the cloth passes through

a series of squeeze rollers while clean hot water is being sprayed on the cloth just prior to each squeezing operation.

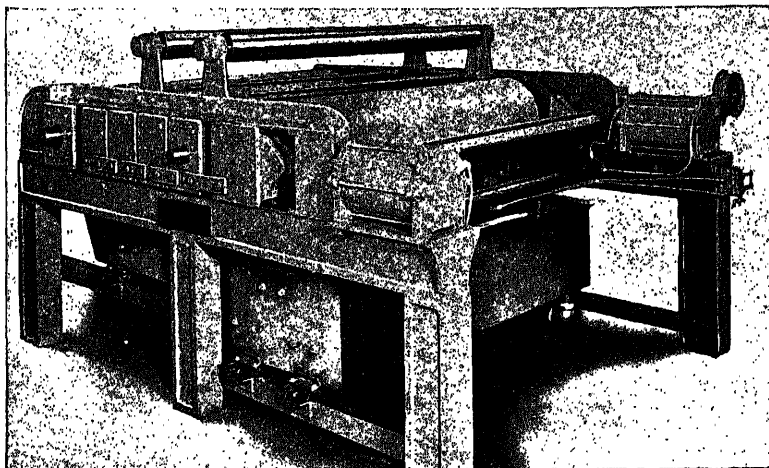
It is advantageous to use hot water (180–190° F.) for the washing as it facilitates the removal of the soluble uncombined materials. A small quan-

*Courtesy of H. W. Butterworth & Sons Company, Philadelphia, Pa.*

Figure 9. Six-roll horizontal washer.

tity of detergent may be employed but it is not necessary as a very satisfactory wash can be obtained by the use of ordinary hot water.

After washing and removal of the excess water the cloth may be dried by any type of drying equipment previously discussed including the loop and air-lay type dryers. The use of a drying frame is, however, recommended as the width of the cloth may be controlled in this type of equipment. To save labor cost and speed production the washing and drying may be combined into one operation by placing the washing equipment directly in front of the drying unit and passing the cloth from the washer to the dryer without interruption.

The flame-resistant fabric may be used as is or it may be given further auxiliary processing such as softening, waterproofing, plastic coating, calendering or sanforizing.

## 2. Double-Bath Precipitation Type

### a. Fundamentals of Processes

*S. Coppick*

Although considerable protection is afforded by the use of certain soluble salts, the very temporary nature of the imparted fireproofing characteristics limits their use in clothing fabrics. The most obvious means for greater permanence lies in the application of insoluble salts. However,

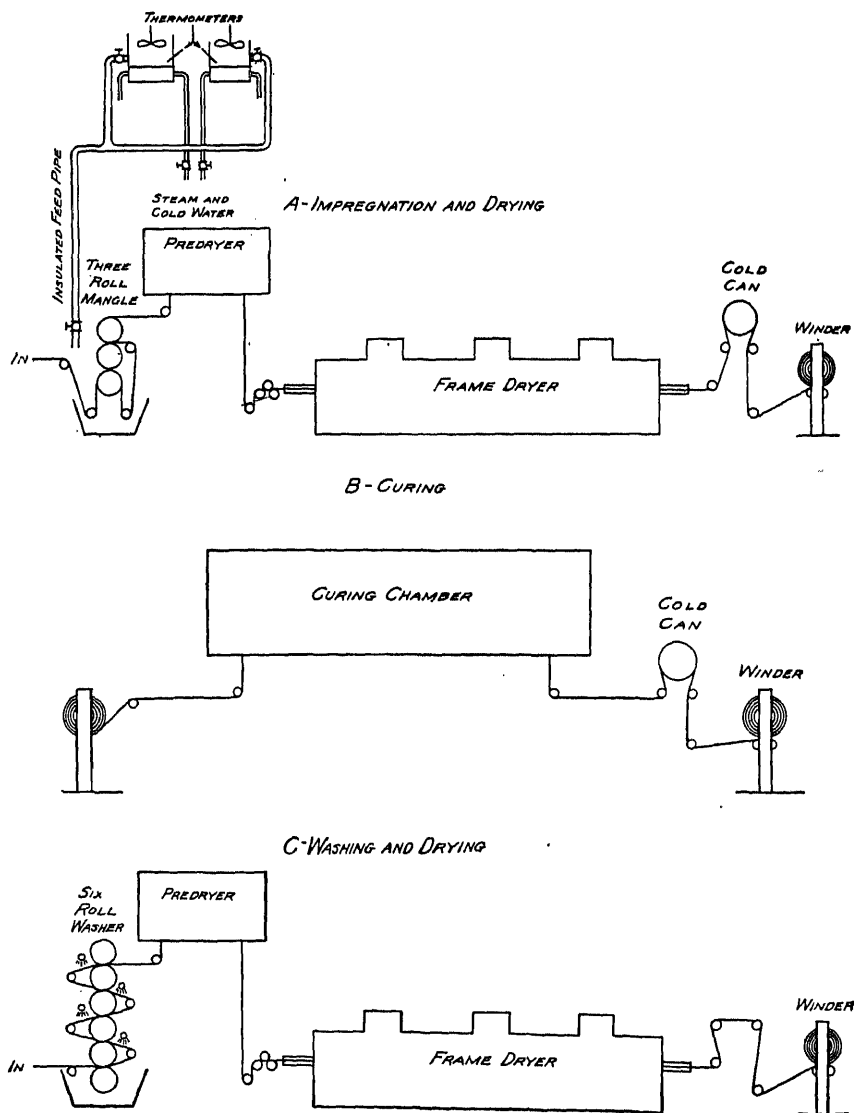



Figure 10. Commercial installation for the processing of fabrics by the urea-phosphate type of treatment.

aside from the technical difficulties, certain fundamental considerations arise here which greatly reduce the number of possible compounds having fire-retarding properties. As has been pointed out in the earlier theoretical sections, the simple salts which impart the desired thermal properties to cellulose embrace those which are capable of easy decomposition at flame temperatures to produce either a strong alkali or a strong acid, and these products are directly responsible for the retardant action. The molecular

instability of the salts of weak acid and strong base or of weak base and strong acid fortunately affords numerous compounds which will undergo the desired thermal decompositions. However, the needed quality of insolubility is generally directly adverse to this thermal instability, the bonding energies which resist ionization and solution also favoring retention of the original molecular state at elevated temperatures. Thus we have the effective action of the soluble ammonium phosphate and the non-retardancy imparted by the calcium salt. Similar radical divergence is exhibited in the effects of ammonium, calcium and barium sulfate and of sodium, calcium and barium carbonate or borate. It is at once apparent that retardancy will be extremely limited for the simple insoluble salts and will be confined to compromises in the field of the amphoteric anions and cations, for instance the phosphates and borates of tin, zinc, aluminum and magnesium, as well as the stannates, tungstates, aluminates, etc.

The greatest possibilities for insolubility combined with efficient fire-retarding qualities lie in the non-salt type, namely the easily reducible hydroxide or hydrated oxides of the metals whose catalytic influence is assumed to direct the course of cellulosic thermal decomposition as previously shown in Chapter III. These include stannic, plumbic, ferric, titanic and chromic oxides as well as those of zinc, cerium, bismuth, tungsten, arsenic and silicon.

Application of both types of these insolubles to cellulose is best carried out by metathetical reactions within the cell wall and lumen of the fiber and in the case of woven fabrics at the fiber to fiber interface in the component yarns and in the interstices between the yarns themselves. Such methods provide for better distribution and location of the retardant as well as serving to support better permanence than the more direct process of attempting to pad these materials into the fabric. It appears also, as will be discussed more fully later, that a more active ingredient may be obtained by precipitations in the cellulose membrane structure.

**Characteristics of Processes.** The reactions are carried out usually via a multi-bath process wherein the fabric is immersed in a solution of a soluble salt containing the desired ion or complex and then dried. The second medium contains the coagulant, which functions either to supply the ionic component required for precipitation, to change the pH, or serve as an oxidant. This latter medium may be either a liquid, vapor or gas, but in the usual case consists of an aqueous solution. The fabric is finally washed, further finishes applied, and dried. The simplest functional process involves a dual impregnation with intermediate drying which leads to the general designation of "Double Bath," although practical applications are sometimes considerably more complicated, multi-components being applied in successive stages.

From the early development of the process by Perkin,[18] numerous for-

[18] Perkin, W. H., U. S. Patent 844,042 (Feb. 12, 1907).

mulations have been proposed and practically all of the known insoluble inorganic compounds have been suggested for retardant purposes. The very nature of the process leads to considerable confusion since the application is indirect and in the majority of cases little if anything is known concerning the actual chemical composition of the material which is precipitated in the fabric from the complex systems used. It is prevalently assumed that such compounds as stannic tungstate, zinc stannate, etc., are the chemical identities affixed to the fiber but from the variable conditions of the precipitations it is much more probable that what is actually obtained consists of complex and variable mixtures of the oxides, hydroxides, and acids of the component metals. Furthermore since many of these amphoteric materials are known to exist as isomorphous mixed crystalline structures in a wide and continuous variety of stoichiometric ratios, even on fundamental grounds they are best considered as their component oxides, particularly in the case of the complex multi-bath formulations. At flame temperatures this is certainly the case.

In systematic studies of the relative efficiencies of a number of insoluble retardants compared with the well-known solubles, Ramsbottom and Snoad [1] came to the conclusion that the multi-bath process is relatively ineffective and state that it is probable that the apparent resulting fireproofed fabric is due largely to the soluble salts absorbed on the precipitated particles and incompletely removed by washing. The add-on requirements for this process are found to be particularly high in most cases compared with the effective but soluble borax-boric acid mixture (Table 17).

Table 17. Relative Efficiencies of Various Insoluble Materials Compared With the Soluble Borate Mixture

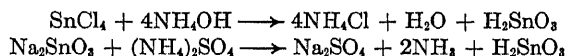
*(Ramsbottom and Snoad [1])*

| | Add-On * % |
|---|---|
| Borax-Boric Acid 1 : 1 | 10 |
| Ferric hydroxide | 25 |
| Antimony oxychloride | 30 |
| Stannic oxide, hydrated | 40 |
| Titanic hydroxide | 40 |
| Bismuth trioxide, hydrated | 40 |
| Zinc stannate | 40 |
| Aluminum borate | 59 |
| Lead peroxide | 60 |
| Cerium hydroxide | 69 |
| Aluminum hydroxide | 70 |
| Chromic hydroxide | 91 |
| Silica, hydrated | 100 |
| Aluminum silicate | 100 |
| Magnesium silicate | 116 |
| Magnesium ammonium phosphate | 125 |

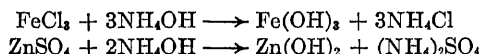
* Minimum quantity necessary to prevent flame propagation.

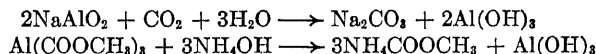
**Impregnation Reactions.** The chemistry of the application of the insoluble materials most commonly entering into flameproofing formulations is as follows:

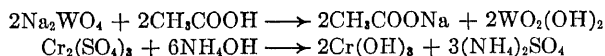
1. The precipitation of stannic acid, *i.e.*, hydrated stannic oxide, is usually carried out by variations of either of two general reactions which involve the alkaline hydrolysis of a stannic salt or the acidification of an alkaline stannate:

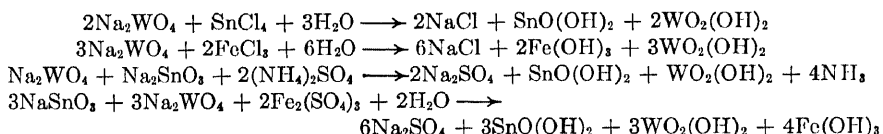
$$SnCl_4 + 4NH_4OH \longrightarrow 4NH_4Cl + H_2O + H_2SnO_3$$
$$Na_2SnO_3 + (NH_4)_2SO_4 \longrightarrow Na_2SO_4 + 2NH_3 + H_2SnO_3$$

Similar neutralization of stannates with ammonium, zinc or aluminum acetate or even acetic acid are also conveniently used.

2. For impregnations with ferric hydroxide, the alkaline hydrolysis of the chloride, sulfate or acetate suffices, as also with zinc:

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$$
$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

3. With alumina, precipitation involves either the acidification of an aluminate or the hydrolysis of the acetate:

$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow Na_2CO_3 + 2Al(OH)_3$$
$$Al(COOCH_3)_3 + 3NH_4OH \longrightarrow 3NH_4COOCH_3 + Al(OH)_3$$

4. In the case of impregnations with tungstic acid, the sodium salt is usually acidified, while chromic hydroxide is brought down from its sulfate by the addition of ammonia:

$$2Na_2WO_4 + 2CH_3COOH \longrightarrow 2CH_3COONa + 2WO_2(OH)_2$$
$$Cr_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Cr(OH)_3 + 3(NH_4)_2SO_4$$

5. Complex systems involving two or more of these reactions are prevalent in the literature, and the products are best considered as the mixed hydroxides rather than such compounds as stannic or ferric tungstate:

$$2Na_2WO_4 + SnCl_4 + 3H_2O \longrightarrow 2NaCl + SnO(OH)_2 + 2WO_2(OH)_2$$
$$3Na_2WO_4 + 2FeCl_3 + 6H_2O \longrightarrow 6NaCl + 2Fe(OH)_3 + 3WO_2(OH)_2$$
$$Na_2WO_4 + Na_2SnO_3 + 2(NH_4)_2SO_4 \longrightarrow 2Na_2SO_4 + SnO(OH)_2 + WO_2(OH)_2 + 4NH_3$$
$$3NaSnO_3 + 3Na_2WO_4 + 2Fe_2(SO_4)_3 + 2H_2O \longrightarrow$$
$$6Na_2SO_4 + 3SnO(OH)_2 + 3WO_2(OH)_2 + 4Fe(OH)_3$$

It is of course obvious that the stoichiometric relations set down by the above equations are the ideal and are dependent primarily upon constant pH relationships which are seldom if ever met with in double-bath precipitations. The actual composition of the hydroxyl compounds laid down in a fabric will depend upon the concentrations and pH at the point location where precipitation takes place. This in turn will depend on the external concentration of the in-filtering second bath and the solution and diffusion rates of that material laid down by the first bath within the fiber.

It is then apparent that the number of individual phases, the composition of these phases and their relative amounts are greatly dependent upon the variables in the process which include concentrations, temperature and time, as well as the presence or absence of pH controlling media such as added acid or base to the second bath. Each of the precipitated phases has a different solution tendency directly proportional to the final pH of the fabric before the washing procedure, so that the reversal of the impregnation proceeds, and the final result is an equilibrium which may be varied widely by suitably setting the conditions of the treatment.

**Recent Developments.** A simplification of the double bath procedure has been advanced by Hopkinson,[19] wherein the primary constituents capable of forming the water-insoluble precipitate are added together to the fabric in an organic solvent. Apparently this solvent should be of sufficient hydrophilic nature to enable wetting of the cellulose and penetration of the constituents, but should have a low enough dielectric constant to prevent precipitation and hold the initial salts in solution molecularly. Such properties appear to be satisfied by both ethylene and diethylene glycol mono-ethyl ether, glycerin, acetamide, triethanol amine and tricresyl phosphate. The insoluble salts of zinc, aluminum, manganese and magnesium may be precipitated in the fiber as the borates, phosphates, tungstates, etc., by first treating the fabric with an organic solution containing the desired ions, drying and finally subjecting the material to water.

This process avoids the difficulties usually encountered in double-bath methods wherein variable precipitating conditions result from changes in concentrations, pH, solubilities and diffusion rates occurring during the second bath impregnation. In the organic solvent treatment the active ingredients are deposited uniformly throughout the fabric and are in intimate contact. The whole of the water-insolubilizing process depends solely upon the inward rate of water penetration in the second bath. A typical example of the method involves the impregnation with a solution of zinc chloride and borax in a glycol solution followed by a water wash to precipitate zinc borate. The use of the organic solvent has the added advantage of permitting the additions of binding resins directly to the first bath.

**Precipitation Conditions.** In extensive experiments performed by the Department of Agriculture,[20] the precipitation conditions appear to be critical factors in determining the flame resistance of treated fabrics. For instance when sodium stannate is precipitated with sulfuric acid rather than with ammonium sulfate as in the Perkin process,[18] a deposit of

[19] Hopkinson, H., U. S. Patent 2,250,483 (July 29, 1941); U. S. Patent 2,343,186 (Feb. 29, 1944).

[20] Leatherman, M., U. S. Dept. of Agriculture, Circular No. 466 (March, 1938).

greater flame-reducing capacity is obtained. Similar improvement is obtained via precipitations carried out with metallic sulfates such as those of copper, chromium, manganese and iron. In these latter treatments an undetermined amount of the metallic hydroxides other than tin remains in the fabric. The mechanism forwarded for the advantage of acid rather than weak base precipitants is that the latter is strongly absorbed on the highly colloidial deposit and poisons its catalytic directionalization of cellulosic dehydration at elevated temperatures.[20]

The use of stannic oxide alone appears to have further disadvantages as pointed out by the British Air Ministry.[1] Fabrics thus treated are extremely sensitive to strength deteriorations in the presence of sunlight. However, in the case of the mixed oxides, this tendering is reduced to a great extent. In the experiments of Leatherman,[20] fabrics exposed outdoors near Washington, D. C. over the months from March to September of 1934 were rendered useless if they contained the stannic oxide alone, were degraded considerably in the presence of stannic and ferric, and remained practically unchanged by the three-component system involving chromic oxide (Table 18). The most effective preserving components are

Table 18. The Sensitivity of Fabrics to Sunlight When Impregnated With Metallic Oxides (6 months' outdoor exposure)

(*Leatherman* [20])

| Treatment | Average Breaking Strength kilo. | Ash Content of Fabric Including Oxides % |
|---|---|---|
| None (unexposed) | 39.3 | 1.0 |
| None (exposed) | 24.9 | 1.0 |
| Stannic Oxide | 2.0 | 7.25 |
| Stannic Oxide + Ferric Oxide | 12.8 | 8.37 |
| Stannic Oxide + Chromium Oxide | 16.7 | 6.27 |
| Stannic Oxide + Ferric Oxide + Chromium Oxide | 24.5 | 9.95 |

those producing a yellow coloration to the fabric and the mechanism is presumed to be the absorption of the active wave lengths.

**Reduction of Afterglow.** Normally metallic hydroxides, although producing adequate flame resistance in a fabric actually enhance its destruction by flameless combustion. The tendency towards glowing in the uncharred area is reduced by the application of chlorinated compounds, but the afterglow of charred regions is still very persistent. Recent experiments by the British[21] show that the insoluble phosphates and borates have little or no flame-retarding properties but inhibit afterglow. Moreover, they are readily removed from the fabric by leaching processes. However, in the case of some tungstates the resistance to both flaming and glowing is fairly good, and the materials are not leached out too easily.

[21] "Fireproofing of Textiles." Interim Report, Chem. Dept., Portsmouth (1945).

The inference is that tungstic acid functions similarly to boric and phosphoric acid to inhibit flameless combustion. Systematic studies on the incorporation of tungstic acid in double-bath precipitation involving stannic and other metallic hydroxides indicate that such is the case. In all flame-retarding systems of stannic, ferric and aluminum hydroxide, the strong glowing tendencies are reduced to either moderate or slight by the inclusion of tungstic acid, which appears to be capable of withstanding considerable water leaching. In the two-component systems involving stannic and another metallic hydroxide, the ferric seems to be the most efficient in its ability to increase the normal protection afforded by the tin alone. Moreover, only very small amounts are necessary, 1% of the iron being sufficient. These effects are shown in Table 19.

Table 19. Effect of Metallic Hydroxides and Acids on the Burning Characteristics of Fabrics

(*Interim Report, Chem. Dept., Portsmouth*[21])

| Hydrated Oxide or Acid | Add-On % | Burning Time (seconds) * Before Leaching | Burning Time (seconds) * After Leaching 48 hrs. Boiling Water | % Loss During Leaching |
|---|---|---|---|---|
| Stannic | 22.5 | 12 | 15 | 3 |
| Stannic + Tungstic | 21.0 | 0 | 15 | 5 |
| Ferric + Stannic + Tungstic | 23.0 | 0 | 0 | 1 |
| Aluminum + Stannic + Tungstic | 24.0 | 55 | 50 | 2.4 |

* Glowing small except for stannic alone.

**General Requirements.** From the above and previous considerations of Chapters II and III, it would seem that the requirements for adequate flame and glow protection in these double-bath treatments are as follows:

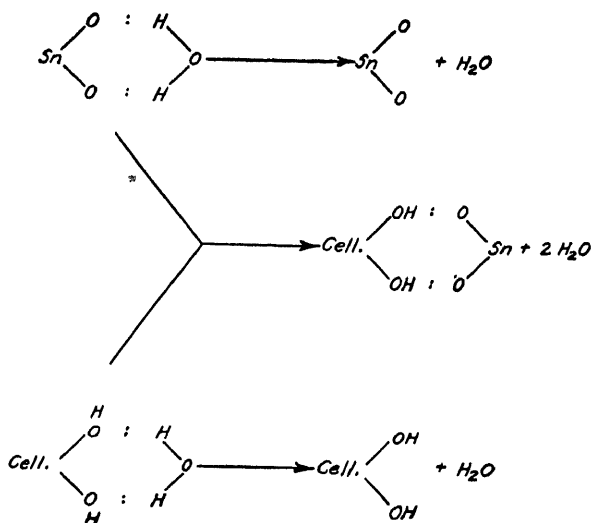
1. A source of a readily reducible metallic oxide or oxide mixture.
2. A source of either boric, phosphoric or tungstic acid.

The oxide may be presumed to function via the chemical mechanisms previously forwarded to prevent afterflaming, while the acid acts as the glowproofing constituent via the fundamental processes set down in the theoretical sections. However, these requirements are stipulated only for the original flameproofed fabric and do not consider the adherence and permanence of the ingredients.

**Durability.** It is well known that the metallic hydroxides and acids are held very tenaciously when dehydrated at cellulose surfaces and there appears to be considerable evidence for interbonding of their normal residual attractive forces with those of cellulose and water which are normally satisfied through hydrogen bridges. The three-component system may be assumed to dehydrate as follows in the regions of cellulosic disorder within as well as on the external surfaces of the fiber:

$$Sn\begin{matrix} O : H \\ O : H \end{matrix}O \longrightarrow SnO_2 + H_2O$$

$$\longrightarrow Cell.\begin{matrix} OH : O \\ OH : O \end{matrix}Sn + 2\,H_2O$$

$$Cell.\begin{matrix} HO : H \\ OH : H \end{matrix}O \longrightarrow Cell.\begin{matrix} OH \\ OH \end{matrix} + H_2O$$

*Schematic reactions for the dehydration of the three-component system: cellulose; stannic oxide; water.*

The system is practically identical with the mordanting of fabrics for various dyeing processes, and may be represented roughly as in Figure 11. Here the moist cellulose and the hydrated oxide are considered as being bound to water molecules through hydrogen bonds. The structures are so

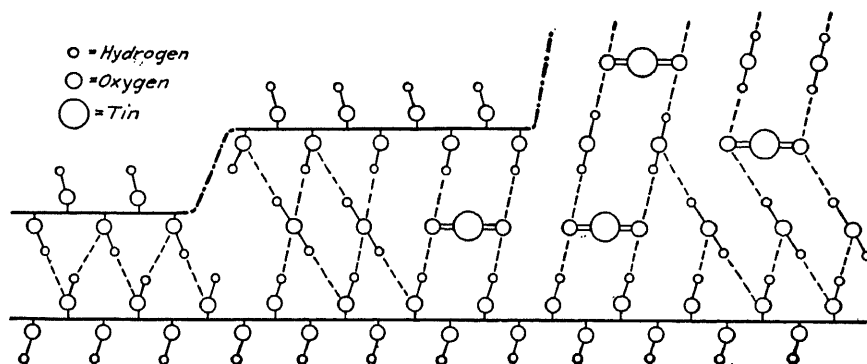
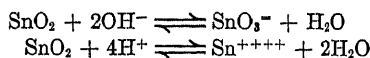



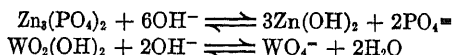
Figure 11. Schematic representation of the possibilities for hydrogen bonding of surfaces in the system cellulose-water-metallic hydroxide.

similar that surfaces may be mutually associated through the same water molecule. On dehydration of the system the free fiber hydroxyls may cellulosate the oxide similar to the normal hydrate structure. The whole of the mechanism depends upon the similarity of space lattices, and the extent to which it will proceed will be determined by favorable inter-atomic distances in the oxide to permit formation of the isomorphous

surface structure. This postulation accounts for the strong adherence in the system and is very probably associated with the actual catalytic dehydration of the flameproofing action.

To further enhance permanence via a mechanical binding of the fire-retarding ingredients to the fiber, resin coatings are frequently applied. These appear to function in the dual role of preventing emulsification of the particles during laundering and to decelerate the solution and diffusion of the ingredients in detergent media. The flameproofing constituents are usually not very susceptible to minor pH changes which would tend to reverse the reaction of their formation, *i.e.*:

$$SnO_2 + 2OH^- \rightleftharpoons SnO_3^{=} + H_2O$$
$$SnO_2 + 4H^+ \rightleftharpoons Sn^{++++} + 2H_2O$$

Thus alkali soaps and acetic acid souring normally cause only a small loss of flame retardancy. However, the anti-glow constituents appear to ionize much more readily, *i.e.*:

$$Zn_3(PO_4)_2 + 6OH^- \rightleftharpoons 3Zn(OH)_2 + 2PO_4^{\equiv}$$
$$WO_2(OH)_2 + 2OH^- \rightleftharpoons WO_4^{=} + 2H_2O$$

By virtue of this, the glow retardancy is poorly retained on laundering.

## b. Laboratory Impregnations

*S. Coppick*

As has been pointed out in the preceding section, the active components of various double-bath formulations may be considered as a glowproofing acid and a flameproofing oxide or oxide mixture. To permit incorporation of these materials in the fabric in various combinations the simplest procedure is to immerse the material first in a solution containing one of the desired radicals, preferably the alkaline salt of the desired acid grouping. When thoroughly wetted out with the reagent the fabric samples are passed through a wringer to remove the excess liquid so that the final wet weight is about twice that of the original dry fabric. The samples are then allowed to dry at room temperature before the second steeping in a solution containing the acidic salt of the desired metallic oxide. Similar wringing and drying procedures are carried out prior to a final leaching treatment in running tap water to remove the excess soluble reagents. The third and last drying process is again conducted at room temperature, after which the fabric is conditioned and is then ready for comparative inflammability evaluation.

A preliminary survey of the relative efficiencies of a number of combinations prepared in this manner is given in Table 20. In a few cases the precipitated phases are retained by the fabric in insufficient quantities to

Table 20. Relative Efficiencies of Various Double-Bath Formulations

| Active Component | | Bath | | | | | Flame Tests | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | No. 1 | | No. 2 | | | Vertical-Bunsen | | 45°-Microburner | | Horizontal-Microburner | |
| Glowproofing Acid | Flameproofing Oxide | Reagent | Conc. % | Reagent | Conc. % | Add-On % | Afterflame sec. | Afterglow sec. | Afterflame sec. | Afterglow sec. | Afterflame sec. | Afterglow sec. |
| None | $Al_2O_3 + SnO_2$ | $Na_2SnO_3 \cdot 3H_2O$ | 10 | $Al_2(SO_4)_3 \cdot 18H_2O$ | 10 | 17.2 | 24 | 82 | 57 | 99 | 70 | 150 |
| None | $ZnO + SnO_2$ | $Na_2SnO_3 \cdot 3H_2O$ | 10 | $Zn(NO_3)_2 \cdot 6H_2O$ | 10 | 30.9 | 23 | 183 | 30 | 276 | 70 | 251 |
| Sulfamic | $SnO_2$ | $NH_4OSO_2NH_2$ | 20 | $SnCl_4 \cdot 5H_2O$ | 20 | 5.2 | 16 | 109 | 59 | 216 | 62 | 77 |
| Boric | $ZnO$ | $Na_2B_4O_7 \cdot 10H_2O$ | 20 | $Zn(NO_3)_2 \cdot 6H_2O$ | 20 | 5.1 | 30 | 39 | 52 | 84 | 45 | 119 |
| Phosphoric | $CaO + P_2O_5$ | $Na_3PO_4 \cdot 12H_2O$ | 20 | $CaCl_2$ | 20 | 18.4 | 30 | 110 | 52 | 312 | 67 | 120 |
| Phosphoric | $Al_2O_3 + P_2O_5$ | $Na_3PO_4 \cdot 12H_2O$ | 20 | $Al_2(SO_4)_3 \cdot 18H_2O$ | 20 | 7.1 | 23 | 58 | 115 | 59 | 59 | 56 |
| Phosphoric | $ZnO + P_2O_5$ | $Na_3PO_4 \cdot 12H_2O$ | 20 | $Zn(NO_3)_2 \cdot 6H_2O$ | 20 | 14.7 | 28 | 31 | 80 | 19 | 94 | 5 |
| Phosphoric | $SnO_2 + P_2O_5$ | $Na_3PO_4 \cdot 12H_2O$ | 20 | $SnCl_4 \cdot 5H_2O$ | 20 | 32.7 | 29 | 3 | 65 | 2 | 66 | 0 |
| Tungstic | $Al_2O_3 + WO_3$ | $Na_2WO_4 \cdot 2H_2O$ | 10 | $Al_2(SO_4)_3 \cdot 18H_2O$ | 10 | 7.1 | 18 | 86 | 136 | 63 | 64 | 77 |
| Tungstic | $Al_2O_3 + WO_3$ | $Al_2(SO_4)_3 \cdot 18H_2O$ | 10 | $Na_2WO_4 \cdot 2H_2O$ | 10 | 24.5 | 22 | 483 | 48 | 6 | 72 | 0 |
| Tungstic | $ZnO + WO_3$ | $Na_2WO_4 \cdot 2H_2O$ | 10 | $Zn(NO_3)_2 \cdot 6H_2O$ | 10 | 30.9 | 19 | 191 | 17 | 206 | 63 | 192 |
| Tungstic | $SnO_2 + WO_3$ | $Na_2WO_4 \cdot 2H_2O$ | 20 | $SnCl_2 \cdot 2H_2O$ | 20 | 29.4 | 0 | 29 | 2 | 33 | 47 | 0 |
| Tungstic | $SnO_2 + WO_3$ | $Na_2WO_4 \cdot 2H_2O$ | 20 | $SnCl_4 \cdot 5H_2O$ | 20 | 31.3 | 0 | 19 | 1 | 11 | 33 | 7 |

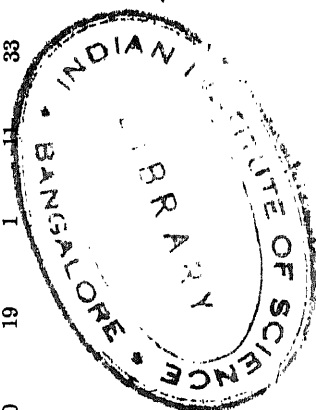



Table 21. The Effect of the Precipitation Conditions in the Stannic Oxide-Tungstic Acid System

| Bath Concentration % | | | | | Flame Tests | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Vertical-Bunsen | | | 45°-Microburner | | | Horizontal-Microburner | | |
| No. 1 $Na_2WO_4 \cdot 2H_2O$ | No. 2 $SnCl_4 \cdot 5H_2O$ | No. of Impregnations | Temperature Bath No. 2 °C. | Add-On % | After-flame sec. | After-glow sec. | Char Length in. | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² |
| 2.5 | 2.5 | 6 | 25 | 32.1 | 26 | 72 | B.E.* | 48 | 12 | B.E. | 63 | 5 | B.E. |
| 5.0 | 5.0 | 4 | 25 | 35.7 | 0 | 13 | 4.7 | 14 | 7 | B.E. | 29 | 3 | 5.9 |
| 10.0 | 10.0 | 2 | 25 | 33.4 | 0 | 18 | 4.6 | 0 | 8 | 3.1 | 7 | 0 | 3.6 |
| 20.0 | 20.0 | 1 | 25 | 31.3 | 0 | 19 | 4.2 | 1 | 11 | 3.6 | 33 | 7 | 5.4 |
| 10.0 | 10.0 | 2 | 100 | 33.2 | 25 | 37 | B.E. | 51 | 6 | B.E. | 62 | 4 | B.E. |
| 10.0 | 10.0 | 2 | 25 | 33.4 | 0 | 18 | 4.6 | 0 | 8 | 3.2 | 7 | 0 | 3.6 |
| 10.0 | 10.0 | 2 | 0 | 35.5 | 0 | 22 | 3.9 | 0 | 5 | 2.6 | 0 | 8 | 2.6 |
| 10.0 | 5.3 | 2 | 25 | 31.2 | 0 | 29 | 4.5 | 1 | 8 | 3.6 | 24 | 6 | 5.8 |
| 10.0 | 5.3 | 2 | 10 | 27.1 | 0 | 15 | 5.0 | 2 | 7 | 3.6 | 34 | 1 | 6.2 |
| 10.0 | 5.3 | 2 | 0 | 28.8 | 0 | 22 | 4.2 | 0 | 9 | 3.2 | 7 | 0 | 4.6 |
| 10.0 | 10.0 | 1 | 0 | 17.6 | 0 | 29 | 4.4 | 13 | 15 | B.E. | 47 | 6 | B.E. |
| 12.5 | 12.5 | 1 | 0 | 20.9 | 0 | 22 | 4.4 | 1 | 15 | 3.0 | 19 | 0 | 4.7 |
| 12.5 | 6.6 | 2 | 0 | 34.3 | 0 | 18 | 3.7 | 0 | 10 | 3.2 | 2 | 5 | 3.0 |
| 20.0 | 10.6 | 1 | 0 | 30.0 | 0 | 17 | 4.0 | 3 | 11 | 3.2 | 6 | 3 | 3.2 |

* B.E.—Burned to the end.

afford any appreciable protection, and it is only when the add-on is in the neighborhood of 25 to 30% that the combinations are truly comparable. Systems in which stannic oxide occurs as one component appear to be most efficient. In combination with phosphoric acid the glow retardancy is very good while with tungstic acid the flaming resistance is best. A compromise with good flame and fair glow resistance favors the tungstic acid-stannic oxide formulation.

**Effect of Precipitation Conditions.** In a more detailed study of this system it seems that the conditions under which the precipitations are carried out have considerable influence on the fire resistance of the final fabric. The procedure of employing numerous impregnations from dilute solutions is not advantageous (Table 21), and usually leads to less protection. The temperature at which the precipitation reaction proceeds also appears to influence the properties, lower temperatures favoring better protection. Table 21 also indicates that the use of a cold second bath permits a lower add-on in the final product. These conditions, however, are not too critical and either a single or double impregnation at room temperature results in products of similar retarding qualities. The most efficient afterglow protection is obtained with an excess of the tungstic acid component, thus favoring high concentrations in the first bath.

**Added Glow Retardants.** Further improvement in glow protection is obtained via the incorporation of the phosphoric radical in the first bath as shown in Table 22. Of the number of combinations attempted, that involving 3% sodium pyrophosphate and 8% sodium tungstate followed by 8% stannic chloride seems to be the most efficient. For adequate protection this process should be carried out twice to result in an addition of about 30% to the original weight of the fabric. However, although the treatment as applied provides the desired resistance to both flame and glow, its permanence to leaching or laundering is very poor. Prolonged immersion in tap water or even very mild washings with neutral detergents appreciably reduce the protective qualities of the fabric (Table 23). With the harsher detergents the resistance to flame and glow is almost totally lost, and it is to be noted that even slight reduction of the add-on below the original 30% causes a marked reduction of the fire resistance.

**Permanence.** The relative ease with which the retardant is removed by leaching or laundering necessitates the additional process of coating the fabric with a binding material. Resins may be applied either as emulsions, solutions in organic solvents or as aqueous dispersions. Table 24 summarizes the results of overcoating fabric previously treated with the stannic oxide-phosphoric-tungstic acid retardant system. In a number of cases the glow retardancy of the fabric is destroyed even by the addition of the binder, while in others the resin appears to be inert. Coatings provide various degrees of retardant retention during treatments in detergent media, and their efficiency is best evaluated via the number of launderings

Table 22. Flame and Glow Retardancy in the Three-Component System Including a Phosphate

| Bath Concentration % No. 1 | | No. 2 | Temperature Bath No. 2 °C. | No. of Impregnations | Add-On % | Flame Test: Vertical-Bunsen | | | Flame Test: 45°-Microburner | | | Horizontal-Microburner | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Na_2WO_4 \cdot 2H_2O$ | Phosphate | $SnCl_4 \cdot 5H_2O$ | | | | After-flame sec. | After-glow sec. | Char Length in. | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow, sec. | Char Area in² |
| 12.5 | 1.0 $Na_3PO_4 \cdot 12H_2O$ | 12.5 | 0 | 1 | 19.8 | 0 | 17 | 4.5 | 1 | 10 | 4.2 | 42 | 5 | 10.7 |
| 5.4 | 4.6 $NaH_2PO_4 \cdot H_2O$ | 5.75 | 25 | 1 | 13.7 | 23 | 2 | B.E.* | 129 | 0 | B.E.* | 49 | 0 | B.E. |
| 7.0 | 3.0 $Na_4P_2O_7 \cdot 10H_2O$ | 10.0 | 25 | 2 | 31.1 | 0 | 7 | 4.9 | 17 | 0 | 3.2 | 20 | 0 | 5.1 |
| 10.0 | 3.0 $Na_4P_2O_7 \cdot 10H_2O$ | 10.0 | 25 | 2 | 44.1 | 0 | 8 | 3.6 | 0 | 3 | 2.5 | 13 | 3 | 3.5 |
| 8.0 | 3.0 $Na_4P_2O_7 \cdot 10H_2O$ | 8.0 | 25 | 2 | 31.2 | 0 | 7 | 4.4 | 2 | 2 | 3.7 | 35 | 0 | 6.3 |

* B.E.—Burned to the end.

Table 23. The Loss of Flameproofness on Leaching and Laundering Fabrics Containing the Stannic Oxide-Phosphoric-Tungstic Acid Retardant

| Solution | Leaching or Laundering Treatment | | | Add-On % | | Flame Test: Vertical-Bunsen | | | Flame Test: 45°-Microburner | | | Flame Test: Horizontal-Microburner | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. of Treatments | Temperature ° F. | Time hrs. | Before Treatment | After Treatment | After-flame sec. | After-glow sec. | Char Length in. | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ |
| None | — | — | — | 31.2 | 31.2 | 0 | 7 | 4.4 | 2 | 2 | 3.7 | 3.5 | 0 | 6.3 |
| 5% NaCl | 1 | 70 | 1 | 31.2 | 28.7 | 6 | 39 | B.E.* | 6 | 23 | 7.2 | 57 | 7 | B.E. |
| Running tap water | 1 | 50 | 72 | 30.3 | 28.8 | 25 | 88 | B.E. | 42 | 89 | B.E. | 65 | 10 | B.E. |
| 0.5% Igepon-T | 1 | 160 | 0.5 | 32.1 | 28.3 | 0 | 7 | 5.2 | 39 | 0 | B.E. | 60 | 0 | B.E. |
| 0.5% Castile Soap 0.2% $Na_2CO_3$ | 1 | 160 | 0.5 | 30.8 | 24.2 | 27 | 88 | B.E. | 46 | 55 | B.E. | 74 | 85 | C.B.** |
| 0.5% Castile Soap 0.2% $Na_2CO3$ | 2 | 160 | 0.5 | 31.2 | 21.7 | 29 | 50 | C.B. | 44 | 116 | B.E. | 74 | 117 | C.B. |

* B.E.—Burned to the end.
** C.B.—Completely burned.

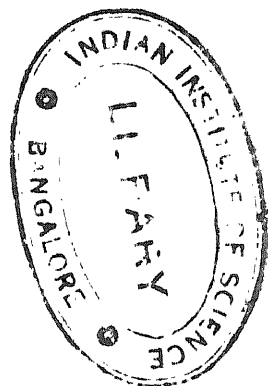



Table 24. The Effect of Resin Overcoatings on the Permanence to Laundering for Fabrics Treated With the Stannic Oxide-Phosphoric-Tungstic Acid Retardant

| Add-On % | | | | | 45°-Microburner Flame Test | | |
|---|---|---|---|---|---|---|---|
| Oxides and Acids | Resin | Total | Resin | No. of Launderings in 0.5% G.I. Soap | Afterflame sec. | Afterglow sec. | Char Area in² |
| 29.0 | 0 | 29.0 | None | 0 | 2 | 2 | 3.7 |
| | | | | 2 | 44 | 116 | C.B.* |
| 23.5 | 11.0 | 34.5 | Casein | 0 | 7 | 215 | C.B. |
| 24.5 | 3.5 | 28.0 | Acetone-Formaldehyde | 0 | 3 | 686 | B.E.** |
| 30.0 | 11.0 | 41.0 | Silica | 0 | 0 | 278 | 2.2 |
| | | | | 1 | 36 | 224 | B.E. |
| 31.8 | 4.2 | 36.0 | Merlon IP-40 | 0 | 0 | 27 | 4.9 |
| | | | | 1 | 35 | 136 | C.B. |
| 31.8 | 17.1 | 48.9 | Cumar MH2½ | 0 | 0 | 18 | 2.1 |
| | | | | 1 | 7 | 34 | 2.3 |
| 23.5 | 4.5 | 28.0 | Urea-Formaldehyde | 0 | 0 | 0 | 2.1 |
| | | | | 3 | 1 | 27 | 3.4 |
| 38.0 | 20.5 | 58.5 | Zelan AP-Methacrol BE | 0 | 0 | 32 | 3.3 |
| | | | | 3 | 0 | 30 | 1.1 |
| | | | | 6 | 39 | 135 | B.E. |
| 26.5 | 5.0 | 31.5 | Phenol-Formaldehyde | 0 | 0 | 0 | 3.1 |
| | | | | 6 | 0 | 0 | 2.9 |
| 31.8 | 1.7 | 33.5 | Resloom M-75 | 0 | 0 | 0 | 3.3 |
| | | | | 6 | 0 | 0 | 2.0 |

* C.B.—Completely burned.
** B.E.—Burned to the end.

necessary to cause excessive flaming or glowing. The most efficient of those investigated are the phenolic and melamine types, both of which enable the fabric to withstand 6 standard launderings in "government issue" soap without any detectable loss of protective qualities as measured by the 45° flame test (Table 24). The quantity of the resin coating necessary for this degree of permanence is rather small and does not add materially to the total weight of the treated fabric. This is particularly true for the melamine type which has a further advantage of not appreciably influencing the hand of the treated fabric.

### c. Industrial Processing

*William P. Hall*

The two-bath application of chemicals to textile fabrics may, in general, be divided into two categories: first, application of chemicals which are not substantive, that is, those which do not have a natural affinity for the fibers; and second, application of chemicals which are substantive, that is, those that have a natural affinity for the fibers. The former include ordinary salts such as sodium chloride, potassium sulfate, sodium sulfonated tallow, etc., and the latter direct dyes, cation active softeners and naphthol base salts, etc.

The successful application of substantive materials involves principles of techniques which will not be discussed in this chapter as the chemicals usually employed in two-bath flameproofing processes are not of this type. It may, however, be understood that if non-substantive chemicals are used which react together on the fabric to form an insoluble product, the second material applied may be said in a sense to be substantive since this chemical is removed from the solution by reacting with the chemical already present on the fiber. The second material may therefore be preferentially removed from the second impregnating bath resulting in a gradual decrease in concentration. This is to some extent similar to the conditions obtained when substantive materials are used and the chemicals are preferentially removed by the fibers thus decreasing the concentration of said chemical in the solution.

These principles are important and should be kept in mind when the two-bath methods of application are used since under these conditions the concentration of the second solution must be continually adjusted in order to obtain a uniformly treated fabric. Methods of minimizing and to some extent overcoming these difficulties will be further described.

The application of chemicals to textile fabrics involving two separate impregnations is therefore not difficult provided the two materials do not have a substantial affinity for each other, that is, do not react together quickly to form new compounds. For example, the impregnation with a

hot solution of sodium pyrophosphate followed by drying and impregnation with a cold solution of ammonium phosphate does not represent a difficult problem since the two do not react quickly to form a new compound. On the other hand the impregnation with a solution of soda ash followed by drying and a second impregnation with magnesium chloride is a difficultly controllable process due to the rapid reaction between the two salts.

If the second component reacts with the first to form an insoluble product the relative quantities of chemicals applied should be so adjusted that a minimum quantity of unreacted chemicals remains on the fabric. It is, however, desirable in certain cases where one component has a detrimental action upon the fiber to insure the presence of an excess of the nontendering component. For example, in the two-bath application of zinc acetate and diammonium hydrogen phosphate the latter component should not be present in excess upon the finished fabric since tendering will result during drying and storage. The excess of diammonium phosphate could be removed by cold water leaching, but this would involve an extra operation.

The mechanical operations involved in two-bath applications may for convenience be divided into two systems. First, those in which the fabric passes without drying from one impregnation directly to the second impregnation; and second, those in which the fabric is partially or completely dried between the first and second immersions. Of these methods the one using complete drying is most easily controlled although it cannot be used where the first component has a detrimental degrading effect when dried into the fibers being processed. The wet method and the one using partial drying are more difficult to control, the latter especially, due to the difficulty in adjusting the fabric to a uniform moisture content prior to the second impregnation.

### *(1) Wet Method of Application*

The most widely used method of size application is by impregnation which in this case means bringing the fabric into contact with the solution and then removing the excess by squeezing through two or more rollers. The type of equipment used for this purpose is usually referred to as a mangle or padder and the process as mangling or padding. A mangle may consist, as already stated, of two, three or more squeeze rollers but only the first two types will be discussed here. In the two-roll mangle the cloth is brought into contact with the solution once by using one or more dips and then squeezed, while in the three-roll mangle the fabric may, if so desired, be dipped into the solution twice and squeezed after each immersion. The squeeze rolls may be of rubber, either natural or synthetic, steel, brass, husk or wood, but usually rubber and steel rolls are used.

The solution boxes attached to the mangles may be of any material not

detrimentally reacted upon by the solution chemicals. Stainless steel is usually preferred. The boxes may have one or more dips so that the cloth may be kept in contact with the solution for a short time before the squeezing takes place. This is important especially where heavy, poorly absorbent fabrics are used or where contact between the fabric and the solution for a certain length of time is necessary to allow a reaction to take place such as may occur in the second solution box when the chemicals in the second solution react with those already present on the fabric.

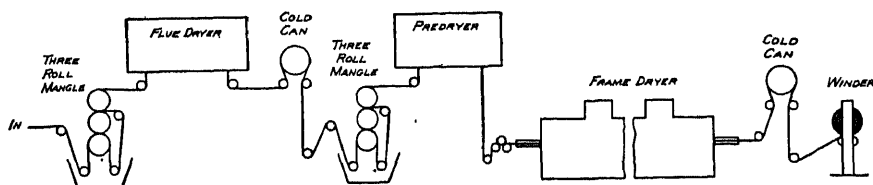



Figure 12. Continuous range for the treatment of fabrics by double-bath processes.

The mangles used in the wet application may be operated separately; for example, the first solution may be applied and the fabric batched in roll form. This wet roll is then taken to a second mangle and the second solution applied. The same mangle may, of course, be used for both impregnations by changing solutions. The process may also be conducted continuously by placing two mangles in tandem and having the cloth pass directly from the first mangle to the second, thus completing both impregnations in one operation.

The squeeze exerted by the two mangles is very important. It is essential that the first mangle exert a heavy squeeze, producing a solution pickup of approximately 50% by weight. The second mangle should then allow an additional 50% pickup from the second bath for a total of 100%. In a process of this type only a short contact with the second solution is necessary in order to obtain the additional 50% solution pickup. It is possible, therefore, to avoid a deep dip into the second bath with the attendant risk of leaching off some of the first component. Contact with the second solution may be accomplished by passing the fabric under a bar just below the surface of the solution or the cloth may pass directly through the squeeze nip. In the latter instance, the lower roll is partially immersed in the bath and serves to bring the solution up to the fabric. In any case, the desired reaction between the two constituents takes place prior to or during drying. From the standpoint of control, this type of application is highly desirable.

As an example of this method, in applying the "Perkin" flameproofing process the concentrations of the sodium stannate and ammonium sulfate solutions are so adjusted that a 50% pickup from each solution assures the proper concentration of chemicals in the cloth. During the subsequent

drying a fine deposit of tin oxide is formed on the fabric leaving only a negligible amount of excess unreacted chemicals.

Another method of wet application may be used with success, provided the chemicals of the first impregnation do not dissolve readily in the second bath but are quickly converted into the insoluble form. It consists in impregnating the fabric with the first solution, using a heavy squeeze if possible, and then bringing the fabric into contact with the second solution for a sufficient time to insure complete combination of the first and second chemicals into the desired compound. The cloth is then finally squeezed before drying. In this case the second bath should be agitated, preferably by an outside circulating pump, to insure uniformity of the solution. A concentrated solution of the chemicals in the second bath should continuously be added into the suction line of the pump and the bath analyzed periodically as a means of maintaining constant composition. This method is not applicable to the Perkin process, where the final insoluble tin oxide is formed during the drying, but only to a process where the final insoluble product is formed in a water medium by precipitation. This method is wasteful since the cloth when leaving the second bath will carry with it a certain quantity of unreacted chemical in addition to that already combined with the chemicals from the first bath.

The equipment used in the final drying operation may be of any conventional textile design such as hot can dryer, flue dryer, loop dryer or frame dryer. Infrared drying lamps or electronic drying may be resorted to but the cost of such methods is prohibitive. In the hot can dryer, the cloth is dried by passing over a series of heated cans; in the flue dryer the cloth passes vertically over a series of rollers inside a drying chamber; in the loop dryer the cloth is hung in a series of loops on bars which move in endless chains inside a drying chamber; in the frame dryer the cloth is held by clips at the selvages under width tension while passing through the drying chamber.

The frame dryer is very desirable since the width of the cloth may be controlled in this machine. Frequently the drying capacity is increased by installing in front of the frame a small number of hot cans or a small flue dryer. This combination constitutes the best equipment available.

The heat may be supplied to these units by steam-heated coils or by direct or indirect gas or oil burners. However, superheated steam coils are the most common source of heat. The cost of electric heating is generally prohibitive.

The temperatures used in the different drying units may vary between wide limits but will usually be between 250° and 350° F. Below 250° F. the drying becomes excessively long and above 350° F. damage to the fabric may result during machine stoppage.

### (2) Dry Method of Application

As previously stated, the dry method may be divided into two categories, those in which the cloth is completely dried between the two impregnations and those in which the cloth is only partially dried.

The first method mentioned is the most reliable of all the double-bath processes since it brings the chemicals in the first bath into intimate contact with the fabric by drying them into the fabric. Also, since the cloth enters both impregnating baths in the dry state, the chemical add-on can be carefully controlled in both applications.

The method is limited in its application by the type of chemicals applied. Thus the process is not adapted to compounds having a deleterious effect when dried upon the fibers, or to compounds which alter their character during drying so that the desired combination with the chemicals in the second bath does not occur.

To obtain uniformity it is recommended that the fabric be cooled to room temperature after the first drying. This is done, first, to insure uniform absorbency when immersing in the second bath; and, second, to prevent the hot dry fabric from overheating the second solution, thus causing non-uniform impregnation and possible decomposition of the chemicals in the bath.

The drying equipment used in the intermediate drying may be the same as that used in the final drying as already described.

As previously stated in the discussion of the wet method, the two impregnations and dryings may be conducted in one, two or several steps. As far as labor cost is concerned, the one-step method is the best. The equipment in this case would consist, for example, of a three-roll impregnating mangle, a flue dryer with cooling attachment, another three-roll impregnating mangle and a drying frame all placed in tandem so that the cloth would enter the first mangle dry in one end and emerge from the frame fully impregnated and dried.

The first impregnation and drying could also be conducted in one step followed by another separate impregnation and drying. The slowest method of operation, and therefore the costliest from the standpoint of labor, consists in dividing the process into four separate operations consisting of two steps each of impregnation and drying. This method of production may, however, be improved by using a high speed impregnation mangle feeding two drying units followed by another similar operation.

The use of the semidrying method is the least desirable of the processes so far described. It follows the same procedure as previously outlined except that the fabric is only partially dried after the first impregnation. In practice it is impossible to adjust the residual moisture content with any

degree of accuracy and it therefore becomes difficult to control the quantity of solution picked up in the second bath. If, however, an insoluble compound is formed quickly on the fiber when the fabric is immersed in the second bath and this conversion is complete or nearly so before leaving the second bath, the degree of moisture present after the preliminary drying is of no great consequence. The loss in chemicals from the second solution would however be excessive since the solution carried out by the cloth from the second bath would contain unreacted chemicals.

In most cases the semidry method is used to insure sufficient pickup in the second impregnation. This, however, can also be accomplished as previously described by using the wet method with 50% pickup in the first impregnation and 100% pickup in the second impregnation.

It is possible with the semidry as with the wet method to use chemicals which have a deleterious effect when dried upon the fibers or which are altered during drying, provided the moisture content during the preliminary drying is kept at a certain minimum value depending upon the chemicals in question. This, however, makes it imperative that the drying procedure be run continuously without interruption as any stoppage would completely dry the material in the dryer. This drawback can be reduced to a minimum by good supervision.

The final drying procedure in the dry as well as the semidry method of application is conducted by methods and with equipment previously described.

The two-bath methods described all use an immersion technique in applying the two solutions and this is the most commonly used procedure. It is also possible, however, to apply the solutions by spraying. In this case such difficulties as changes in concentration and composition of the second solution may be eliminated. In some cases both solutions may be applied by spraying or, better still, the first solution is applied by immersion and the second solution by spraying.

The spray method has however some serious drawbacks which make it impractical for large-scale production except in very special cases. These are, first, the penetration obtained is poor, especially in heavy fabrics; second, it is difficult to control the quantity of solution applied and the uniformity of deposit; and, third, the wastage of solution is generally excessive.

The two-bath processes described presuppose the use of aqueous solutions to dissolve or disperse the chemicals. Lately, however, a method has been developed which employs a water-soluble organic solvent medium in the first bath rather than water. This allows the mixing of the two components together with other chemicals in the same solution without the required reactions taking place. The solution is applied by immersion and then usually dried. This is followed by a second immersion in water where the reaction between the two components takes place forming the desired

insoluble product. It is also possible to include in the aqueous second bath additional constituents which contribute to the flameproofing or, as in the case of special resinous treatments, impart a greater degree of permanence to the finish. In like manner, other desirable characteristics such as water repellency may be introduced at this stage of the finishing process.

As an example of this type of process, one of the durable flame-resistant treatments which has been employed commercially in this country [19] makes use of a glycol ether solution of zinc chloride and sodium borate. After immersion in this first bath the deposition of the insoluble reaction products can be achieved by a second immersion in an aqueous medium or by allowing slow hydrolysis and double decomposition to occur in the course of exposure of the treated fabric to humid atmospheric conditions. For practical reasons and to serve as an illustration of the type of process under consideration, it may be assumed that the immersion in the organic solvent solution is followed directly by a second aqueous bath.

This type of flameproofing treatment possesses the disadvantages of increased costs in using an organic solvent in place of water in the first bath and the fact that the regular textile equipment commonly employed commercially is not particularly well adapted to handle organic solvent solutions.

In this section an effort has been made to present the general techniques used in the application of two-bath flameproofing processes. With slight modification either one or the other of these methods may be used depending upon the chemicals and reactions involved. The two-bath methods of obtaining durable or semidurable flameproofing properties have been little used in this country until recently, one reason being the lack of interest and requisition for durable flameproofing finishes. In England, however, the need for such properties in textiles was early recognized and there the two-bath processes have been extensively employed.

## 3. Metallic Oxide-Chlorinated Body Type

### a. Fundamentals of Processes

*S. Coppick*

The use of metallic oxides alone as fireproofing agents as advocated by Perkin *et al.*[18,22,23] suffers from several disadvantages. In the first place these treatments are not permanent in the ordinary sense of the word

[22] Perkin, W. H., Proc. Eighth Int. Cong. Applied Chem., 28, 119 (1912); Quar. Nat'l. Fire Prot. Assn. 6, 179 (1912); Nat'l. Fire Prot. Assn. Educ. Bul. D 37 (Boston, 1912).

[23] Perkin and Bradbury, Brit. Patents 17814, 17815 (1913); Perkin and Whipp Bros., and Tod, Brit. Patents 9695, 23557 (1901), 6421, 8509, 9620 (1902), 24222 (1903), 22169 (1904).

since they usually lose their retardant qualities fairly rapidly on leaching and laundering. The second disadvantage is the enhancement of the flameless combustion characteristics which the oxides impart to cellulose.

In efforts to offset these features which limit the application of the process, numerous formulations have been proposed for combinations of the metallic oxides with other materials. The function of the extra components is presumed to include the mechanical bonding of the pigment to the fiber, to aid in its practical application, to decrease the abnormal glowing tendencies which accompany the oxide treatment, to improve the hand or color and to inhibit the tendering encountered during weathering or storage. Of the large number of ingredients advocated, the main component appears to be the binder. This is generally a resinous substance which in itself has little or no flaming tendencies and most commonly is either a chlorine addition or substitution product such as polyvinyl chloride, the copolymer of vinyl chloride and vinyl acetate, chlorinated paraffin, diphenyl, naphthalene, or certain halogen substitution products or carbocyclic compounds. The mechanism whereby these materials contribute to the flame and glow-retarding tendencies is assumed to be either in their coating properties to exclude oxygen or their ability to produce hydrogen chloride at flame temperatures to dilute the ambient combustible atmosphere. The combination of the metallic oxide with the chlorinated body is thought[24] to be particularly advantageous since the former is presumed to act catalytically as a dechlorinating agent to promote rapid hydrogen chloride production at temperatures in the vicinity of that at which fabric decomposition ensues.

**Studies of Individual Components.** The system on which the most recent and extensive practical efforts have been directed is that involving antimony oxide and a chlorinated body. It would appear that since this process is of such practical interest and considerable information is available on its industrial application and actual performance, it would be ideal as a basis for fundamental investigations. Such appears to be the case also from an experimental point of view, since the individual components alone appear to be practically inactive in retardant action while certain combinations are very effective. It is therefore possible to study the system without the added complication of varied summative effects.

In fundamental studies on the three-component system: cellulose-antimony oxide-chlorinated body, it is at once apparent that as many as possible of the interdependent variables should be eliminated. Thus application of combinations by direct emulsion or solvent treatments are hazardous since each of the components may influence the state and location of the other. A simpler attack is to apply them separately so that

[24] Leatherman, M., Major, C.W.S., Memorandum Report, T.D.M.R. No. 936, Army Service Forces, Office, Chief, Chemical Warfare Service, Edgewood Arsenal, Md. (Dec. 2, 1944).

component and combination effects may be considered on the same basis. This is accomplished conveniently by impregnation of fabrics with the oxide via a dispersion in 2% aqueous methyl cellulose, the binder having been shown to exert an effect similar to an equal added quantity of cellulose itself. The chlorinated body is applied as a solution in an organic solvent such as carbon tetrachloride, trichlorethylene or acetone, and combinations of the two components are added to fabrics both in the above or in the reverse order.

Investigations on the components alone indicate that the antimony oxide has only a slight flame-retarding effect on cotton fabric. Although capable of eliminating afterflaming in the mild vertical test only for very high additions, the oxide exhibits no appreciable retardation of flaming when measured by the more drastic 45° and horizontal testing procedures. Similarly, chlorinated paraffins of various chlorine contents and vinylites have only slight retarding effects when added to fabrics. For the most part they simply reduce slightly the rate at which flame is propagated, as shown in Table 25.

Table 25. The Effect of Various Chlorinated Materials and Their Combinations With Antimony Oxide on the Flaming Characteristics of Fabrics

*(Approximately 40% add-on and weight ratios of 1 : 1)*

| Retardant Component | Chlorine Content % | | Afterflaming (secs.) Vertical | 45° | Horizontal | Flame Rate in./sec. 45° |
|---|---|---|---|---|---|---|
| None | — | —— | 30 | > 60 | > 60 | 0.86 |
| Antimony oxide | 0 | alone | 0 | 40 | > 60 | 0.57 |
| Pentachlorodiphenyl | 54 | alone | 35 | > 60 | > 60 | 0.37 |
| | | combined | 0 | 9 | > 60 | 0 |
| Neoprene | 40 | alone | 35 | 45 | 59 | 0.56 |
| | | combined | 0 | 1 | 0 | 0 |
| Chlorinated paraffin | 42 | alone | 60 | > 60 | > 60 | 0.81 |
| | | combined | 0 | 0 | 21 | 0 |
| Chlorinated paraffin | 70 | alone | 42 | > 60 | > 60 | 0.81 |
| | | combined | 0 | 0 | 0 | 0 |
| Vinylite | 50 | alone | 60 | > 60 | > 60 | 0.65 |
| | | combined | 0 | 0 | 0 | 0 |
| Aniline hydrochloride | 27 | alone | 38 | > 60 | > 60 | 0.32 |
| | | combined | 0 | 0 | 0 | 0 |

With combinations of the two materials, however, the retardation is very effective. For a given addition of the chlorinated body there exists a minimum add-on requirement of $Sb_2O_3$ to limit the afterflaming to zero in each of the three flame tests. It is seen further that the relative efficiencies of the chlorinated materials are in direct proportion to their

ease in liberating hydrogen chloride when they alone are pyrolyzed in contact with the fabric (Table 26).

Table 26. The Effect of the Acid-Producing Capacity of the Chlorinated Body on the Add-On Requirements for Effectively Flameproofing Cotton Fabrics with Antimony Oxide Combinations

| | Chlorinated Body | | | Antimony Oxide Requirement % for Zero Afterflaming | | |
|---|---|---|---|---|---|---|
| Type | Chlorine Content % | Add-On % | Acid Generated milli. equiv. wts. per in $^2$ of fabric | Vertical | 45° | Horizontal |
| Paraffin | 42 | 10.8 | 0.09 | 14.2 | 26.0 | > 54 |
| Vinylite | 50 | 13.7 | 0.33 | 8.6 | 8.6 | 12.4 |
| Paraffin | 70 | 15.1 | 0.47 | 7.4 | 12.5 | 7.4 |

**Nature of Acid Donors.** Halogen-containing compounds other than those normally used behave similarly, combinations of antimony oxide with neoprene, aniline hydrochloride, ethylene diamine hydrochloride, aniline hydrobromide and ammonium chloride being much more effective than either of the components alone. These acid-producing bodies, however, seem to be limited to the halogen type, since sulfuric acid donors such as aniline sulfate do not exhibit nearly so marked retarding qualities.

The nature of the chlorinated compound in respect to the ease with which it liberates hydrogen chloride seems to be critical in these combinations. The tendency appears to be dependent upon several factors: the initial chlorine content, the volatility of the compound at flame temperatures, and the nature of the chlorine bond, as determined by its attachment to either an aromatic or aliphatic carbon. Thus the highly chlorinated waxes and the vinylites are particularly good from their potentially and actually available hydrogen chloride in that they remain in contact with the fabric for sufficient time at flame temperatures to permit their efficient thermal decomposition, while the lower chlorinated oils produce low hydrogen chloride yields due to their volatility. However, it appears that mixtures of the wax and oil type of chlorinated paraffin are sufficient to give the required retention at flame temperatures without the undesirable hand characteristics imparted by either of the constituents. By appropriate proportioning of these two, high available hydrogen chloride may be maintained without excessive oily or boardy products resulting. The flame-retarding efficiencies of these blends are shown in Table 27. Chlorine on a double bonded carbon is well known to have quite stable thermal characteristics which impart poor retardancy to the combinations of the chlorinated diphenyls with antimony oxide. This coincides with the observed fact that here only 3% of the chlorine content is readily thermally available while in the vinylites or highly chlorinated paraffins this value may be as high as from 40 to 60% (Table 28).

**Optimum Ratio.** Variation in the ratio of the oxide to the chlorinated body indicates that there exists an optimum which extends over a con-

Table 27. The Effect of Blending Chlorinated Paraffins on Their Flame-Retarding Efficiencies When Combined with Antimony Oxide

| Antimony Oxide Add-On % | Chlorinated Paraffin Chlorine Content % | Chlorinated Paraffin Add-On % | Afterflaming* sec. 45° | Afterflaming* sec. Horizontal |
|---|---|---|---|---|
| 7.8 | 42 | 5.8 | 18 | > 60 |
| 8.0 | | 15.9 | 0 | > 60 |
| 8.2 | | 31.1 | 0 | > 60 |
| 8.3 | 70 | 4.6 | 0 | > 60 |
| 6.6 | | 17.8 | 0 | 2 |
| 7.4 | | 30.0 | 0 | 0 |
| 8.2 | 42–70 | 6.6 | 11 | 59 |
| 6.9 | (Blend 1 : 1) | 17.0 | 0 | 2 |
| 7.5 | | 28.6 | 0 | 0 |
| 18.5 | 42 | 3.9 | 58 | 46 |
| 19.3 | | 8.3 | 12 | 58 |
| 19.6 | | 15.5 | 1 | 8 |
| 17.4 | 70 | 5.9 | 1 | 7 |
| 19.1 | | 7.6 | 0 | 6 |
| 18.9 | | 15.8 | 0 | 0 |
| 20.4 | 42–70 | 4.1 | 60 | 53 |
| 22.8 | (Blend 1 : 1) | 8.9 | 0 | 6 |
| 17.0 | | 15.6 | 0 | 1 |

* Vertical afterflaming zero in all cases.

Table 28. The Thermal Availability of Hydrochloric Acid from Fabrics Treated With Various Chlorinated Materials

| Chlorinated Body Type | Chlorine Content % | Add-On % | Hydrochloric Acid Available % Theoretical | Hydrochloric Acid Available % From Pyrolysis | Fraction Thermally Available |
|---|---|---|---|---|---|
| Diphenyl | 54 | 35.6 | 14.7 | 0.9 | .061 |
| | | 40.7 | 15.9 | 0.5 | .03 |
| | | 50.0 | 18.6 | 0 | 0 |
| Paraffin | 42 | 10.4 | 4.2 | 0.7 | .17 |
| | | 12.1 | 4.7 | 1.1 | .24 |
| | | 19.4 | 7.0 | 1.7 | .24 |
| | | 24.9 | 8.6 | 3.5 | .41 |
| | | 30.6 | 10.1 | 4.2 | .41 |
| | | 35.0 | 11.1 | 2.5 | .23 |
| | | 43.1 | 13.0 | 4.6 | .35 |
| | | 51.0 | 14.6 | 3.7 | .25 |
| Paraffin | 70 | 7.7 | 5.1 | 1.3 | .25 |
| | | 11.5 | 7.6 | 4.9 | .66 |
| | | 18.3 | 11.7 | 6.3 | .54 |
| | | 26.0 | 15.7 | 8.7 | .55 |
| | | 30.8 | 18.2 | 10.9 | .60 |
| | | 39.6 | 22.2 | 12.5 | .56 |
| | | 49.3 | 24.1 | 14.4 | .55 |
| | | 50.3 | 27.7 | 15.1 | .55 |

siderable range, the value of which seems to depend not on the theoretically but the actually available hydrogen chloride from the chlorinated body. Thus for a wax containing 70% chlorine the optimum extends from a $\frac{Sb_2O_3}{C.P.}$ weight ratio of about 1 to 3, which includes the theoretical value of 2.7 for an equal atomic ratio of chlorine to antimony. The practically available ratio, since only about 50% of the potential hydrogen chloride is produced thermally from fabric treated with this wax and pyrolyzed at 500° C., is 1.35 which is quite close to the practical minimum ratio of 1.0 as shown in Figure 13. It appears also that this optimum ratio is inde-

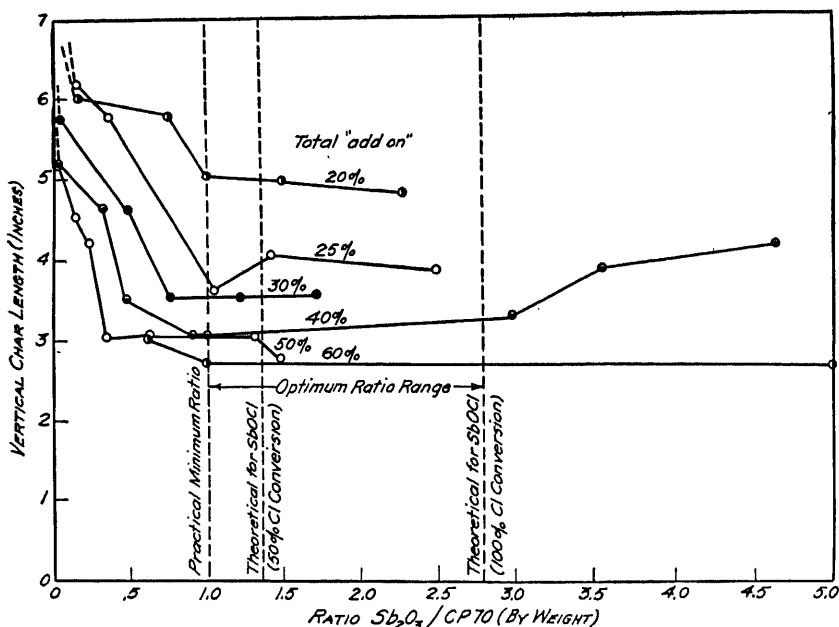



Figure 13. Variation in flame-retarding performance as a function of the component ratio and the total add-on for the system including a 70% chlorinated paraffin.

pendent of the total addition of the combination to the fabric, increasing amounts reducing the flaming tendencies markedly for add-on values of from 20 to 30%, and thereafter much more slowly.

**Added Glow Retardants.** In the four-component systems including cellulose, antimony oxide, a chlorinated body, and a glow retardant, it is more convenient for fundamental studies to utilize a hydrochloric acid donor of high capacity. Aniline hydrochloride seems to be ideal for this purpose since at flame temperatures the dissociation is almost complete. Furthermore, it is practically inert as far as flame and glow retardancy are concerned when it is applied alone to the fabric. However, in combination with antimony oxide the flameproofing is excellent while the glowing

proceeds as in the absence of the hydrochloric acid donor. This compound is of course of no practical value in fireproofing formulations due to its water solubility, but it permits studies in the multi-component systems without additive glow-retarding effects and eliminates considerations of possible catalytic dechlorination by the metallic oxide.

Studies on retardant mixtures involving antimony oxide, aniline hydrochloride and a borate are summed up in Table 29, where it is seen that

Table 29. Summarized Flame and Glow-Retardant Effects in the System Including Antimony Oxide, Aniline Hydrochloride and a Borate

| Original Component | | | | Flame-proofing | | Glow-proofing | | |
|---|---|---|---|---|---|---|---|---|
| Antimony Oxide | Aniline Hydrochloride | Boric Acid | Zinc Borate | Good | Poor | Good | Poor | Proposed Active Components * |
| × | | | | | × | | × | |
| | × | | | | × | | × | |
| | | × | | | × | × | | Boric Acid |
| | | | × | | × | | × | |
| × | × | | | × | | | × | Antimony Oxychloride |
| | × | × | | | × | × | | Boric Acid |
| | × | | × | Fair | | × | | Zinc Chloride + Boric Acid |
| × | | × | | | × | × | | Boric Acid |
| × | | | × | | × | | Fair | |
| × | × | × | | × | | × | | Antimony Oxychloride + Boric Acid |
| × | × | | × | × | | × | | Antimony Oxychloride + Zinc Chloride + Boric Acid |

* The proposed active product directly responsible for the effects is given in the last column.

although many of the components have no appreciable retarding effects, their mixtures are effective in both flame and glowproofing characteristics. In the light of the known flame-retarding qualities of zinc chloride and antimony oxychloride[1] when applied alone to fabrics and the anti-glow properties of boric acid, the proposed active ingredients in the system are given in the table.

The action of antimony oxychloride may be demonstrated by direct application of this rather unstable compound or by precipitating it in a fabric by partial hydrolysis of antimony trichloride. In the borate system

it is seen that the theoretical ratio for the formation of antimony oxychloride coincides with the minimum flaming tendencies of fabrics treated with the combination while the anti-glow characteristics also favor this ratio as shown in Figure 14. Similar experiments with the four-component

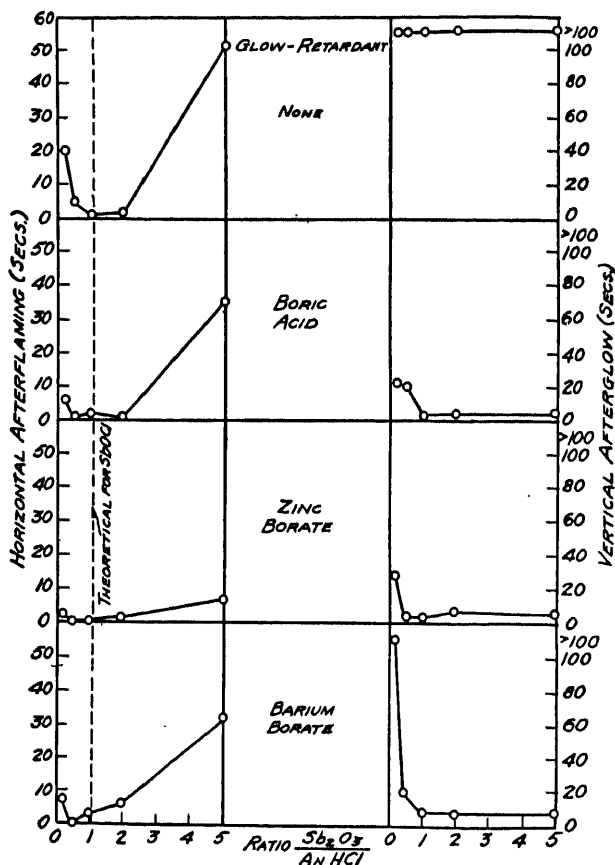



Figure 14. The efficiencies of various ratios of oxide to aniline hydrochloride in both flame and glow retardancy for a 35% add-on which includes 5% of a borate as the anti-glow constituent.

system including a phosphate glow retardant lead to a similar optimum ratio of one atom of antimony per atom of available chlorine. Here it appears that the addition of sodium phosphate does not improve the glowing characteristics, but "mild-base" phosphates such as diammonium phosphate or zinc ammonium phosphate reduce the glowing tendencies to practically nil (Table 30).

Table 30. The Efficiencies of Various Phosphates as Anti-Glow Agents When Used With the Antimony Oxide-Aniline Hydrochloride 1 : 1 Flame-Retarding System

| Glow Retardant | Total Add-On % | Vertical Test * Afterglow sec. | Vertical Test * Char Length in. |
|---|---|---|---|
| None | 35.8 | > 100 | 3.0 |
| 5% Trisodium Phosphate | 33.4 | > 100 | 3.0 |
| 5% Zinc Ammonium Phosphate | 37.0 | 7 | 2.7 |
| 5% Diammonium Phosphate | 39.0 | 3 | 2.6 |

* Afterflaming zero in all cases.

**General Requirements.** From the above it is proposed that the requirements for effective flameproofing and glowproofing in this system are:

1. Antimony oxide.
2. A source of hydrochloric acid.
3. A source of either boric acid or phosphoric acid.

The mechanism via which the practically useful formulations fulfill these requirements is presumed to be as follows:

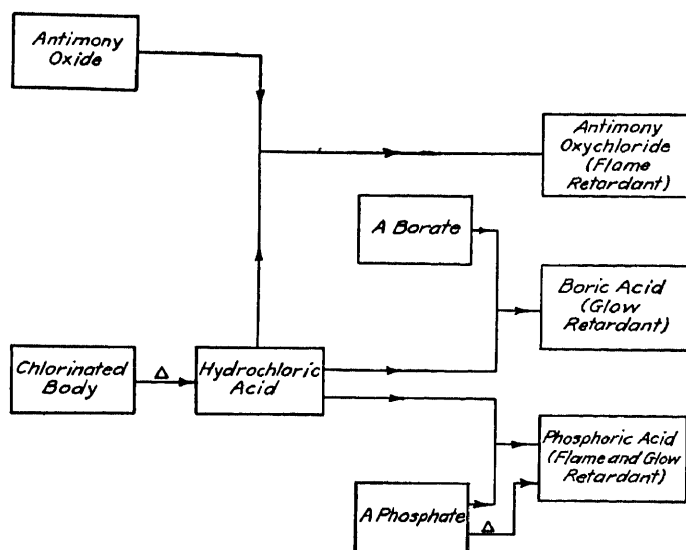



*Diagram of proposed mechanism for system: $Sb_2O_3$, chlorinated body, glow retardant.*

Glowproofing components are limited to those substances which will produce one of the two acids either by thermal decomposition or by double decomposition in the presence of hydrochloric acid, and the final active

components must function in their flame- and glow-retarding actions by the chemical mechanisms forwarded in the previous chapter. However, the number of practical examples of good dual retarding properties in this system are limited by the lack of insoluble compounds which will undergo these reactions.

The proposed mechanisms are substantiated by kinetic considerations of the reactions which lead to the formation of antimony oxychloride. Optimum conditions which theoretically should lead to its high instantaneous concentration on the fabric actually show maximum flame-retarding efficiencies. However, these considerations propose homogeneous reactions which are only rough approximations for the multiphase heterogeneous practical formulations. The mean retardancy should actually depend upon the effective concentration of the active component at any given point location on the fiber surface. In the limit this rests on the state of division of the pigment and its uniform application to the fabric. With solvent treatments the chlorinated wax or oil is quite intimately in contact with the fiber so that the main factor is the pigment. Here it is obviously more expedient to use higher rather than lower ratios in order to ensure adequate effective coverage with antimony oxychloride, as demonstrated in Figure 13. In the case of emulsion applications, both of the components are heterogeneously applied so that the characteristics of the dispersion become critical. Thoroughly homogenized and stable preparations should favor better performance. However, irrespective of the method of application, this system of flameproofing inherently suffers from the high add-on disadvantage since it depends upon the yields from several consecutive reactions between heterogeneously applied phases. Such reactions are well known for their sluggishness.

All of the above considerations pertain solely to the original flame- and glow-retarding characteristics of the treated fabrics, and do not consider their permanence to laundering. The removal of the flame-retarding constituents takes place only slowly by mechanical and emulsification processes brought about by detergents, while the anti-glow reagent is usually lost by solution. To minimize this removal with its consequent deterioration of protective properties it is apparent that it will be necessary to stray somewhat from the ideal formulations in order to provide greater adherence and decelerate diffusion processes. Consideration is given to these factors in the following section.

### b. Laboratory Impregnations

*Robert W. Little*

In the preceding section of this chapter the fundamental aspects of the antimony oxide-chlorinated wax type of flameproofing treatment have

been discussed outlining the variables existent in the flameproofing mixture and in the more complex formulations required for proper application to the fabric. The laboratory investigations which aid in the evolution of these theories and lend support to their claims are presented in the following pages.

### *(1) Fundamental Investigations*

**Study of Separate Components.** In a system as complex as these emulsion or suspension mixtures it is highly desirable to investigate the functions of the flameproofing ingredients separately without the complications of the vehicle components. Since it is known that the flame-retarding mechanism concerns itself with the metallic oxide and the chlorinated body only, a series of experiments were performed in which these two components were applied to the fabric alone and in combination with each other. The pigment was added to the fabric as a suspension in methyl cellulose, it having been found that the latter had no apparent effect upon the flaming characteristics of cotton fabrics. The chlorinated resin or wax was applied as a solution in a suitable organic solvent which could be removed from the fabric by drying. The results of these investigations have been summarized in Table 31 showing several different ratios of two components and various add-ons of individuals and mixtures. Antimony oxide when applied alone displays no significant flame-retardant activity even at add-ons as high as 53%. Similarly, in most cases, the acid-forming materials investigated do not in themselves possess flame-retarding properties. The exceptions to this are ethylene-diamine dihydrochloride, ammonium chloride and aniline hydrobromide. When added to the fabric together, antimony oxide and the acid donors show an efficient flame-retarding action and a ratio of approximately 1 : 1 appears to be most effective in the majority of cases. Deviations on either side of this ratio have been found to require higher add-ons to achieve comparable retardancy.

**Acid Donors.** A comparison of the acid-bearing materials gives some insight into the desirable characteristics of this component of the flameproofing mixture. Of the chlorinated bodies considered, the most effective are aniline hydrochloride, 70% chlorinated paraffin and Vinylite VYNS, in that order. The 42% chlorinated paraffin, neoprene and the aroclors are shown to be less effective in approximately the order listed. When mixed with antimony oxide, ethylenediamine dihydrochloride and the ammonium chloride exhibit a high degree of retardancy but considerations of their relative effectiveness is obscured by the flame-resisting properties which they possess in their own right. The effectiveness of other inorganic acids in the flameproofing system under discussion is indicated by the results obtained with aniline hydrobromide and aniline sulfate. Apparently the

Table 31. Flameproofing Efficiency of Antimony Oxide and Various Acid-Producing Materials, Alone and in Combination

(*45°-Microburner Flame Test*)

| Materials Added and Ratio of Mixture | | Total Add-On % | After-flame sec. | After-glow sec. | Char Area in $^2$ | Flame Rate in./sec. (45°) |
|---|---|---|---|---|---|---|
| Antimony Oxide | 42% Chlorinated Paraffin | | | | | |
| 1 | 0 | 5.6 | 52 | > 100 | C.B.* | .68 |
| 1 | 0 | 18.9 | 58 | > 100 | C.B. | .61 |
| 1 | 0 | 37.6 | > 60 | > 100 | C.B. | .58 |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 51.0 | completely consumed | | | .75 |
| 0.8 | 1 | 19.6 | 10 | > 100 | B.E.** | 0 |
| 2.0 | 1 | 32.2 | 1 | > 100 | 3.2 | 0 |
| 5.0 | 1 | 65.0 | 0 | > 100 | 2.4 | 0 |
| Antimony Oxide | 70% Chlorinated Paraffin | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 50.3 | 55 | 0 | C.B. | .54 |
| 0.4 | 1 | 20.8 | 59 | > 100 | C.B. | .66 |
| 1.5 | 1 | 37.7 | 0 | > 100 | 1.9 | 0 |
| 3.8 | 1 | 72.3 | 0 | > 100 | 1.9 | 0 |
| Antimony Oxide | Vinylite VYNS | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 31.5 | completely consumed | | | .65 |
| 0.35 | 1 | 18.5 | 0 | > 100 | 3.1 | 0 |
| 1.2 | 1 | 30.6 | 0 | > 100 | 2.6 | 0 |
| 3.6 | 1 | 63.5 | 0 | > 100 | 2.4 | 0 |
| Antimony Oxide | Neoprene | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 59.7 | 45 | 0 | B.E. | .56 |
| 1 | 2 | 29.0 | 0 | > 100 | 2.6 | .57 |
| 1 | 1.8 | 38.6 | 1 | 0 | 2.1 | 0 |
| 2.7 | 1 | 60.2 | 0 | 3 | 1.9 | 0 |
| Antimony Oxide | Aniline Hydrochloride | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 36.5 | > 60 | 0 | B.E. | .32 |
| 1 | 5 | 22.4 | 21 | > 100 | B.E. | .50 |
| 1 | 2 | 21.0 | 0 | > 100 | 5.3 | 0 |
| 1 | 1 | 25.5 | 0 | 6 | 4.2 | 0 |
| 2 | 1 | 36.3 | 0 | > 100 | 4.1 | 0 |
| 4 | 1 | 77.4 | 0 | 10 | 3.7 | 0 |

Table 31 (*cont'd.*)

Flameproofing Efficiency of Antimony Oxide and Various Acid-Producing Materials, Alone and in Combination

(*45°-Microburner Flame Test*)

| Materials Added and Ratio of Mixture | | Total Add-On % | After-flame sec. | After-glow sec. | Char Area in $^2$ | Flame Rate in./sec. (45°) |
|---|---|---|---|---|---|---|
| Antimony Oxide | Ethylenediamine Dihydrochloride | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 19.2 | 58 | — | B.E. | .27 |
| 0 | 1 | 33.6 | 4 | — | 3.0 | 0 |
| 0 | 1 | 44.4 | 0 | — | 2.5 | 0 |
| 1 | 1 | 23.0 | 4 | — | 3.9 | 0 |
| 2.2 | 1 | 20.7 | 1 | — | 3.6 | 0 |
| 3 | 1 | 21.8 | 0 | — | 3.4 | 0 |
| Antimony Oxide | Aroclor 1254 | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 50.0 | > 60 | — | C.B. | .33 |
| 1 | 1 | 25.6 | 9 | — | 4.9 | 0 |
| 2.25 | 1 | 27.9 | 14 | — | 7.4 | 0 |
| 3 | 1 | 41.0 | 9 | — | 4.3 | 0 |
| Antimony Oxide | Aroclor 1270 | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | .44 |
| 0 | 1 | 11.3 | > 60 | — | C.B. | .55 |
| 1 | 1 | 24.5 | > 60 | — | B.E. | .50 |
| Antimony Oxide | Ammonium Chloride | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | 0.44 |
| 0 | 1 | 23.4 | 25 | — | B.E. | 0.12 |
| 0 | 1 | 32.0 | 0 | 0 | 2.9 | 0 |
| 1 | 1 | 13.7 | 4 | — | 3.5 | 0 |
| 1 | 1 | 25.8 | 0 | — | 2.1 | 0 |
| Antimony Oxide | Aniline Sulfate | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | 0.44 |
| 0 | 1 | 19.4 | 23 | — | B.E. | 0.38 |
| 1 | 1 | 27.1 | > 60 | 0 | B.E. | 0.45 |
| Antimony Oxide | Aniline Hydrobromide | | | | | |
| 1 | 0 | 53.0 | 41 | > 100 | C.B. | 0.44 |
| 0 | 1 | 8.3 | 6 | — | 5.7 | 0 |
| 0 | 1 | 14.4 | 0 | 0 | 5.4 | 0 |
| 0.84 | 1 | 14.5 | 0 | > 100 | 5.3 | 0 |
| 0.84 | 1 | 36.8 | 0 | 6 | 3.1 | 0 |

* C.B.—Completely burned.

** B.E.—Burned to the end.

other halogen acids would function similarly to hydrochloric though interpretation of the results obtained with the hydrobromide is complicated by the efficiency of the salt when present alone. The limited data available on comparable sulfates suggest that sulfuric acid does not function nearly as efficiently in this particular flameproofing mechanism as do the halogen

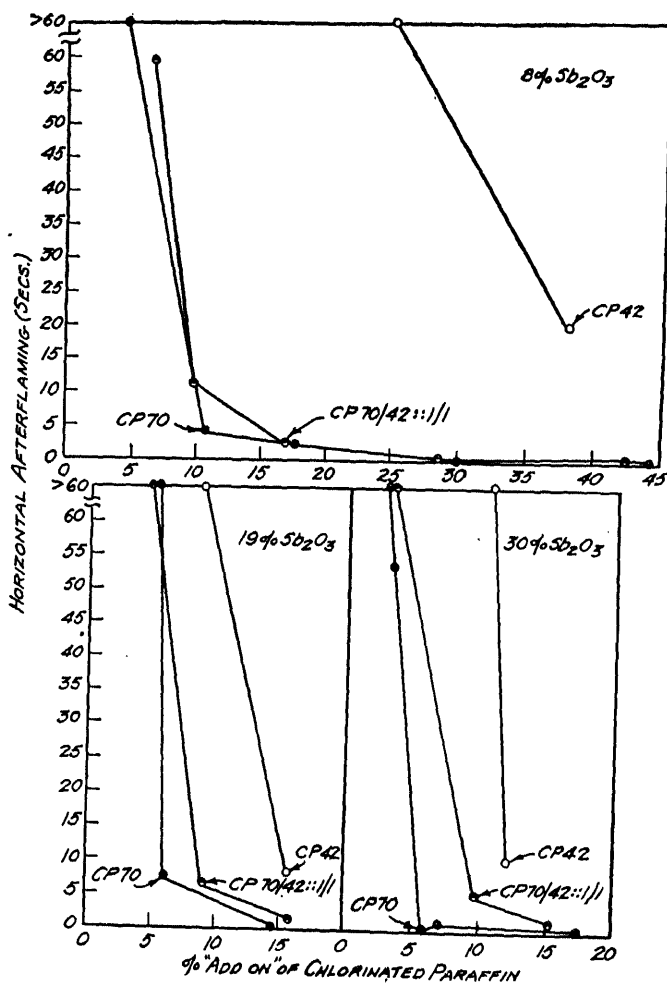



Figure 15. Effect of blending chlorinated paraffins on their flame-retardant efficiency with antimony oxide.

acids. Since the flameproofing mechanism is assumed to be the reaction of antimony oxide with hydrochloric acid at elevated temperature, forming antimony oxychloride, the true flameproofer, the amount of acid present and the availability when required would seem to be a possible explanation for the differences in performance demonstrated in Table 31.

This has been found to be true as illustrated by the data shown in Table 28. Supplementary to this, aniline hydrochloride which is the most effective of the materials tested also contains an adequate supply of hydrochloric acid which is even more readily available. Obviously, in addition to containing sufficient hydrochloric acid in a readily available form, the chlorinated constituent must also be sufficiently non-volatile to allow it to remain on the fabric at the elevated temperature for a period long enough to permit the release of the acid.

**Function as Binders.** In addition to serving as a source of the acid required in the flameproofing reaction, the wax or resin also functions as a binder to cement the solid constituents to the fabric and improve the permanence of the treatment. The importance of this function will be apparent in later considerations of the emulsion and suspension treatments. Using a 40% chlorinated paraffin in conjunction with antimony oxide the resultant treated fabric possesses good hand characteristics but the retardancy obtained is of relatively low order and is subject to removal by leaching and laundering treatments. With mixtures of 70% chlorinated paraffin and antimony oxide, however, the treated fabric is more effectively flameproofed and more resistant to leaching action but the fabric is stiff and boardy. In an attempt to reach a compromise of flame retardancy, permanence and hand characteristics, blends of the two chlorinated paraffins were employed in the flameproofing mixture. It was thought that the 40% material would serve in the capacity of a plasticizer for the solid wax of higher chlorine content and yet the mixture still retain some of the desirable properties of available acid and resistance to detergent action. The curves of Figure 15 bear out this expectation, the mixture being much superior to the 42% chlorinated paraffin in flame-resistant activity. Later data will indicate that it is also more effective in resisting leaching and laundering and preserving the hand characteristics of the untreated fabric.

### *(2) Practical Formulations*

#### (*a*) *Oil-in-Water Emulsions*

After fundamental consideration of the function of the flameproofing components the problem remains to arrive at a practical formulation for effectively applying the mixture to the fabric. Due to the simplicity of adaptation to commercial finishing practices the first laboratory applications were attempted in the form of an oil-in-water emulsion. In order to secure an emulsion sufficiently stable to allow its use in an application of this type, several variations in composition were required, mainly the incorporation of a diluent, emulsifying agent and stabilizer into the mixture. In the early investigations, 42% chlorinated paraffin was used due to its favorable viscosity, ammonium oleate was selected as the emulsifying

Table 32. Variations in the Stability of Antimony Oxide-Chlorinated Paraffin Oil-in-Water Emulsions

| Composition of Emulsion (parts by weight) | | | | | | Stability |
|---|---|---|---|---|---|---|
| Chlorinated Paraffin (42%): Antimony Oxide (1:1.6) | Solvesso #2 | Oleic Acid U.S.P. | Conc. Ammonium Hydroxide | Methyl Cellulose (4% soln., H.V.) | Water | Separation in 2 days at 21° C.; % by volume |
| 40 | 0 | 4 | 4 | 0 | 52 | 51.4 |
| 40 | 0 | 6 | 6 | 0 | 48 | 3.0 |
| 40 | 2.5 | 4 | 4 | 0 | 49.5 | 48.0 |
| 40 | 2.5 | 6 | 6 | 0 | 45.5 | 8.8 |
| 40 | 5 | 4 | 4 | 0 | 47 | 38.8 |
| 40 | 5 | 6 | 6 | 0 | 43 | 3.2 |
| 40 | 7.5 | 4 | 4 | 0 | 44.5 | 30.6 |
| 40 | 7.5 | 6 | 6 | 0 | 40.5 | 0.0 |
| 40 | 10 | 4 | 4 | 0 | 42 | 30.2 |
| 40 | 10 | 6 | 6 | 0 | 38 | 0.0 |
| 40 | 0 | 4 | 1 | 4 | 46 | 43.6 |
| 40 | 0 | 5 | 1.25 | 4 | 45.75 | 46.2 |
| 40 | 2.5 | 4 | 1 | 4 | 46 | 29.2 |
| 40 | 2.5 | 2 | 0.5 | 4 | 46.5 | 41.7 |
| 40 | 5 | 4 | 1 | 4 | 46 | 1.3 |
| 40 | 5 | 2 | 0.5 | 4 | 46.5 | 40.9 |
| 40 | 7.5 | 4 | 1 | 4 | 46 | 0.0 |
| 40 | 7.5 | 2 | 0.5 | 4 | 46.5 | 27.2 |
| 40 | 10 | 4 | 1 | 4 | 46 | 0.0 |
| 40 | 10 | 2 | 0.5 | 4 | 46.5 | 7.7 |
| 40 | 5 | 4 | 0.25 | 8 | 42.75 | 32.9 |
| 40 | 5 | 4 | 0.5 | 8 | 42.5 | 4.2 |
| 40 | 5 | 4 | 0.7 | 8 | 42.3 | 2.4 |
| 40 | 5 | 4 | 1.0 | 8 | 42.0 | 1.1 |
| 40 | 5 | 4 | 1.3 | 8 | 41.7 | 11.8 |
| 40 | 5 | 4 | 2 | 8 | 41 | 18.2 |
| 40 | 5 | 4 | 3 | 8 | 40 | 25 |

agent and methyl cellulose as a stabilizer. The effect of variations in these ingredients upon the stability of the emulsion obtained are summarized in Table 32. On the basis of these experiments the following formulation was derived for a stable emulsion:

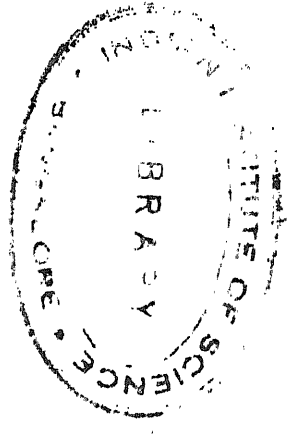
| | |
|---|---|
| Chlorinated paraffin (42%)-antimony oxide | 40 parts |
| Light petroleum fraction (Solvesso #2) | 5 " |
| Oleic acid | 4 " |
| Conc. ammonium hydroxide (28–29%) | 1 " |
| Methyl cellulose (H.V., 4% in $H_2O$) | 4 " |
| Water | 46 " |

**Optimum Ratio.** The ratio of chlorinated paraffin to antimony oxide in the pigment was originally set at 1:1.6 which was calculated to be theoretical for the quantitative conversion of antimony to antimony oxychloride. Realizing that this method of application might influence the

Table 33. Variations in the Flameproofing Efficiency of Antimony Oxide-Chlorinated Paraffin Oil-in-Water Emulsions with Changing Ratios of Chlorinated Paraffin to Antimony Oxide

| Ratio of Chlorinated Paraffin (42%) to Antimony Oxide | Initial Add-On % | Residual Add-On After 3 Launderings in 0.5% G.I. Soap | Flameproofness * — Horiz. Microburner Test | | | | Flameproofness * — 45°-Microburner Test | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Before Laundering | | After 3 Launderings | | Before Laundering | | After 3 Launderings | |
| | | | Afterflame sec. | Char Area in² | Afterflame sec. | Char Area in² | Afterflame sec. | Char Area in² | Afterflame sec. | Char Area in² |
| 1 : 2 | 28.0 | 21.5 | 53 | B.E.** | 61 | B.E. | 0 | 3.4 | 15 | B.E. |
| | 35.7 | 22.7 | 5 | 2.5 | 77 | B.E. | 0 | 2.2 | 5 | 6.5. |
| | 40.8 | — | 3 | 2.5 | — | — | 0 | 2.3 | — | — |
| 1 : 1.6 | 19.5 | 7.4 | 61 | B.E. | 47 | B.E. | 27 | B.E. | 47 | B.E. |
| | 25.8 | 15.7 | 22 | 6.3 | 75 | B.E. | 1 | 3.7 | 1 | 6.2 |
| | 34.1 | 18.2 | 1 | 4.1 | 79 | B.E. | 1 | 4.6 | 3 | 5.8 |
| 1 : 1.2 | 26.2 | 17.6 | 57 | B.E. | 48 | B.E. | 1 | 3.7 | 31 | B.E. |
| 1 : 1 | 27.8 | 15.9 | 4 | 3.5 | 85 | B.E. | 0 | 2.7 | 5 | 4.9 |
| 1.2 : 1 | 32.1 | 17.4 | 0 | 3.9 | 94 | B.E. | 0 | 3.9 | 3 | 5.3 |
| 2 : 1 | 27.6 | 12.7 | 53 | B.E. | 49 | B.E. | 0 | 4.4 | 32 | B.E. |

* Afterglow times are not given since the afterglow was greatly excessive in all cases and showed no consistent trends with the changes in composition.

** B.E.—Burned to the end.

effectiveness of the flameproofing ingredients, either due to improper particle size or poor distribution in the fabric, the influence of the ratio of the metallic oxide to the wax was investigated when added in the above emulsion. It was found, as shown in Table 33, that an optimum ratio was approximately 1:1 rather than the 1:1.6 originally arrived at by theoretical considerations. This is in agreement with the findings of Table 28, *i.e.*, that only a fraction of the chlorine content of the chlorinated paraffin is readily available as hydrochloric acid at flame temperatures.

**Addition of Glow Retardants.** One of the principal criticisms of this general type of flameproofing treatment, particularly with respect to its use on clothing fabrics, was the highly excessive afterglow which occurred in all cases. In an attempt to reduce or prevent this glowing reaction, several different glow-retarding compounds of restricted solubility were incorporated in the emulsions. The general formulation used in preparing these emulsions was the same as that previously given, the glow retardant being added in partial substitution of the oxide-wax pigment. As indicated by the data of Table 34, none of the materials investigated was completely effective but a considerable improvement was achieved particularly in the case of zinc borate and phenyl diamidophosphate. The addition of the glow-retarding constituent reduced the stability of these emulsions somewhat and variations in the emulsifying agent used or the amount of stabilizer present did not significantly improve the stability. In attempting to increase the amount of glow retardant added, the stability was impaired to such an extent that the emulsion could no longer be applied to the fabric.

### (*b*) *Water-in-Oil Emulsions*

In order to achieve greater stability and also allow the addition of more of the glow retardants, a water-in-oil emulsion was developed. The composition of subsequent emulsions of this type was as follows:

| | |
|---|---|
| Water | 50 parts |
| 42% Chlorinated paraffin-antimony oxide (1 : 1) | 28 " |
| Glow retardant | 5 " |
| Light petroleum fraction (Solvesso #2) | 12 " |
| Rezyl | 5 " |

In these experiments also, the data of which are summarized in Table 35, zinc borate and phenyl diamido phosphate were the only glow retardants tested which materially improved the afterglow of the emulsion-treated fabric. The efficiency of the additional amounts of glow retardant in the water-in-oil emulsions was no greater than the smaller amounts in the emulsions with water as the external phase. The stability was markedly improved, however, and made effective impregnation easier.

**Variations of Metallic Oxide.** Many metallic oxides, other than antimony oxide, have been reported to be effective in preventing after-

Table 34. Incorporation of Glow Retardants in Antimony Oxide-Chlorinated Paraffin Oil-in-Water Emulsions *

| Glow Retardant | No. of Launderings in 0.5% G.I. Soap | 45°-Microburner Flame Test: Total Add-On % | Afterflame sec. | Afterglow sec. | Char Area in² | Vertical-Bunsen Flame Test: Total Add-On % | Afterflame sec. | Afterglow sec. | Char Length in. |
|---|---|---|---|---|---|---|---|---|---|
| Melamine Pyrophosphate | 0 | 27.8 | 0 | 8 | 2.6 | 29.6 | 0 | 14 | 4.5 |
| | 3 | | 0 | 243 | 3.4 | | 0 | 374 | 4.7 |
| Zinc Borate | 0 | 34.1 | 0 | 0 | 2.8 | 30.9 | 0 | 21 | 4.5 |
| | 3 | | 0 | 0 | 4.3 | | 0 | 368 | 5.5 |
| Phenyl Diamido Phosphate | 0 | 37.4 | 0 | 11 | 4.4 | 37.0 | 0 | 20 | 4.5 |
| | 3 | | 0 | 0 | 3.7 | | 0 | 446 | 5.0 |
| Zinc Ammonium Phosphate | 0 | 35.5 | 0 | 100 | 4.0 | 36.3 | 0 | 159 | 4.7 |

* All glow retardants added in the amount of 1.5 parts/100 parts of emulsion.

Table 35. Incorporation of Glow Retardants in Antimony Oxide-Chlorinated Paraffin Water-in-Oil Emulsions *

| Glow Retardant | No. of Launderings in 0.5% G.I. Soap | 45°-Microburner Flame Test: Total Add-On % | Afterflame sec. | Afterglow sec. | Char Area in² | Vertical-Bunsen Flame Test: Total Add-On % | Afterflame sec. | Afterglow sec. | Char Length in. |
|---|---|---|---|---|---|---|---|---|---|
| Zinc Borate | 0 | 36.0 | 0 | 8 | 2.5 | 35.6 | 0 | 14 | 4.5 |
| | 3 | | 0 | 2 | 2.8 | | 0 | 284 | 4.5 |
| Phenyl Diamido Phosphate | 0 | 33.5 | 0 | 10 | 3.8 | 34.1 | 0 | 23 | 5.0 |
| | 3 | | 0 | 278 | 3.8 | | 0 | 487 | 6.7 |
| 50% Phosphated Polyvinyl Alcohol | 0 | 37.8 | 0 | 145 | 4.0 | 37.6 | 0 | 350 | 5.2 |
| Zinc Phosphate | 0 | 31.3 | 0 | 243 | 2.8 | 30.0 | 0 | 294 | 6.0 |
| Stannic Phosphate | 0 | 24.7 | 0 | 178 | 4.8 | 24.1 | 0 | 244 | 6.0 |
| Cupric Phosphate | 0 | 28.7 | 0 | 176 | 4.1 | 27.5 | 0 | 54 | 5.0 |
| Ferric Phosphate | 0 | 35.1 | 0 | 166 | 5.4 | 34.9 | 0 | 276 | 6.0 |

* All glow retardants added in the amount of 5 parts/100 parts of emulsion.

Table 36. Variation of the Metallic Oxide Component of the Antimony Oxide-Chlorinated Paraffin Water-in-Oil Emulsions *

| Flame Retardant | Total Add-On % | No. of Launderings in 0.5% G.I. Soap | Horizontal-Microburner Flame Test | | | 45°-Microburner Flame Test | | |
|---|---|---|---|---|---|---|---|---|
| | | | Afterflame sec. | Afterglow sec. | Char Area in² | Afterflame sec. | Afterglow sec. | Char Area in² |
| Antimony Trioxide ($Sb_2O_3$) | 36.0 | 0 | 2 | 2 | 2.2 | 0 | 8 | 2.5 |
| | | 3 | 2 | 2 | 1.8 | 0 | 3 | 2.8 |
| Antimony Pentoxide ($Sb_2O_5$) | 25.4 | 0 | 48 | 0 | B.E.** | 50 | 0 | B.E. |
| Antimony Trioxide : Antimony Pentoxide ($Sb_2O_3 : Sb_2O_5$ :: 1 : 1) | 30.9 | 0 | 0 | 0 | 2.2 | 0 | 0 | 3.4 |
| | | 3 | 0 | 0 | 2.2 | 0 | 0 | 3.2 |
| Antimony Trioxide : Antimony Oxytrichloride ($Sb_2O_3 : SbOCl_3$ :: 1 : 1) | 30.2 | 0 | 1 | 4 | 2.9 | 0 | 3 | 2.9 |
| | | 3 | 3 | 4 | 3.2 | — | — | — |
| Zinc Oxide ($ZnO$) | 37.7 | 0 | 35 | 0 | B.E. | 0 | 18 | 5.5 |
| | | 3 | 37 | 0 | B.E. | 0 | 5 | 5.7 |
| Antimony Trioxide : Zinc Oxide ($Sb_2O_3 : ZnO$ :: 1 : 2) | 35.7 | 0 | 28 | 0 | B.E. | 0 | 0 | 3.4 |
| | | 3 | 0 | 0 | 3.4 | 0 | 0 | 4.1 |
| Stannic Oxide ($SnO_2$) | 34.1 | 0 | 48 | 0 | B.E. | 55 | 35 | B.E. |
| Manganese Dioxide ($MnO_2$) | 33.0 | 0 | 47 | 187 | B.E. | 43 | 185 | B.E. |

* All emulsions contain 5% zinc borate and 20 parts/100 of the flame retardant.

** B.E.—Burned to the end.

flaming in flameproofing mixtures of this type. Using the same formulation given above, a series of water-in-oil emulsions were prepared substituting other materials in whole, or in part, for antimony oxide. The results of these experiments as presented in Table 36 indicate that antimony pentoxide, zinc oxide, stannic oxide and manganese dioxide are inferior to antimony trioxide in the prevention of afterflaming, at least when applied in this manner. A 1:1 mixture of antimony trioxide with the pentoxide or oxytrichloride is equal to or better than the trioxide alone. A similar mixture of antimony trioxide with zinc oxide in the ratio of 1:2 is not as effective in the prevention of afterflaming but appears to be superior in its glow-preventing properties.

**Variations of Chlorinated Body.** Since the experiments portrayed in Figure 15 indicated that a mixture of the 70% and 42% chlorinated paraffins would be superior to the 42% product alone and also because of the distinct advantage of the mixture with respect to the hand of the fabric, a series of emulsions were prepared and tested in which the mixture replaced the 42% material. The data presented in Table 37 indicate a slight improvement in flame resistance and a much more striking increase in both the efficiency and permanence of the glow retardancy achieved. A similar emulsion in which the 42% chlorinated paraffin was replaced with Vinylite VYNS displayed flameproofing properties superior to the low chlorine content paraffin alone and slightly inferior to the mixture of the two paraffins. This is again in agreement with the proposition that the effectiveness of the oxide-chlorinated body mixture is dependent, at least in part, upon the amount of hydrochloric acid available and the ease with which it may be released. In order to obtain a satisfactory emulsion in this case the composition had to be altered as follows:

| | |
|---|---|
| Water | 28.5 parts |
| Vinylite VYNS | 5.7 " |
| Triphenyl phosphate | 6.8 " |
| Antimony oxide | 6.8 " |
| Zinc borate | 3.4 " |
| Rezyl | 3.4 " |
| Dichloroethane | 45.4 " |

The dichloroethane was substituted for the light petroleum fraction in order to effect solution of the copolymer chloride-acetate resin and triphenyl phosphate was required to plasticize the relatively stiff fabric obtained from the resin treatment. It is possible that with the amount of plasticizer added, the phosphate may have contributed somewhat to the effectiveness of the treatment.

**Variations of Solvent.** With the thought that the use of a volatile and highly inflammable solvent in a process of this type might constitute a hazard in the average finishing plant, attempts were made to replace the petroleum fraction with a non-inflammable diluent such as carbon tetra-

Table 37. The Effect of Blending Chlorinated Paraffins of Different Chlorine Content in the Antimony Oxide-Chlorinated Paraffin Water-in-Oil Emulsions*

| Chlorinated Paraffin Used | Total Add-On % | No. of Launderings in 0.5% G.I. Soap | Flame Test | Afterflame sec. | Afterglow sec. | Char Area, in² or Char Length, in. |
|---|---|---|---|---|---|---|
| | 36 | 0 | Horiz. | 2 | 2 | 2.2 |
| | | 3 | " | 2 | 2 | 1.7 |
| 14 pts. — 42% C.P. | 36 | 0 | 45° | 0 | 8 | 2.5 |
| | | 3 | " | 0 | 2 | 2.8 |
| | 35.6 | 0 | Vert. | 0 | 14 | 4.5 |
| | | 3 | " | 0 | 284 | 4.5 |
| | 36.5 | 0 | Horiz. | 0 | 0 | 2.3 |
| | | 3 | " | 0 | 0 | 2.3 |
| 4 pts. — 70% C.P.<br>8 pts. — 40% C.P. | 36.5 | 0 | 45° | 0 | 0 | 3.4 |
| | | 3 | " | 0 | 0 | 2.7 |
| | 38.8 | 0 | Vert. | 0 | 6 | 4.0 |
| | | 3 | " | 0 | 58 | 4.0 |

* Both emulsions contain zinc borate to the extent of 5 parts/100 parts of emulsion.

chloride. Using the mixture of chlorinated paraffins which had proven itself to be more effective than either used separately, the following emulsion was prepared:

| | |
|---|---|
| Water | 44.2 parts |
| Chlorinated paraffin (42%) : antimony oxide (1 : 1) | 16.0 " |
| Chlorinated paraffin (70%) | 3.6 " |
| Zinc borate | 5.3 " |
| Rezyl | 4.4 " |
| Carbon tetrachloride | 26.5 " |

Comparisons with fabric treated with standard emulsion containing solvesso showed no appreciable difference between the two preparations before or after six laboratory launderings.

In the course of the laboratory experimentation with the emulsion type of flameproofing treatment it was found that adjustment of the add-on obtained could be more easily made by variations in the pressure of the squeeze rolls than by attempting to vary the concentration of the emulsion. The minimum effective add-on for this treatment was found to be in the neighborhood of 30%. To insure sufficient impregnation and adequate coverage the add-on should be slightly above 30%. Lower additions of the retardant mixture led to inconsistencies in the effectiveness of the treatment, particularly with respect to the permanence of the retardancy. Applications to both regular 8.5 oz. herringbone twill and the same fabric after all traces of sizing had been removed by an enzymatic and scouring treatment showed that there was no apparent difference in the effectiveness of the impregnations obtained. As was pointed out in the earlier sections on the urea-phosphate type of process, the effectiveness of the treatment in that case was greatly dependent upon the absorbency of the fabric.

**Most Satisfactory Formulation.** As a result of the experimentation just considered, the following formulation was selected as representing the most effective mixture for the application of the antimony oxide-chlorinated paraffin flameproofing agent in the form of an emulsion:

| | |
|---|---|
| Water | 50.0 parts |
| Antimony oxide | 11.3 " |
| Chlorinated paraffin (42%) | 5.7 " |
| Chlorinated paraffin (70%) | 3.8 " |
| Zinc borate | 5.7 " |
| Rezyl | 4.7 " |
| Trichloroethylene * | 18.8 " |

This water-in-oil emulsion was applied to 8.5 oz. herringbone twill by small-scale commercial techniques and the efficiency of the flameproofness

* The light petroleum fraction was replaced by trichloroethylene in order to avoid the hazard of inflammability. The tests carried out on the treated fabric indicate that in this particular instance the effectiveness of the treatment with this solvent was slightly inferior to that normally obtained with the petroleum solvent.

Table 38. Substitution of 40% Chlorinated Paraffin and 70% Chlorinated Paraffin for Vinylite VYNS in the Antimony Oxide-Vinylite Solvent Suspension Treatment

| Vinylite : Chlorinated Paraffin Ratio | Glow Retardant | Total Add-On % | No. of Launderings in 0.5% G.I. Soap | 45°-Microburner Flame Test | | | Vertical-Bunsen Flame Test | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Afterflame sec. | Afterglow sec. | Char Area in² | Afterflame sec. | Afterglow sec. | Char Length in. |
| VYNS : 40% C.P. (1 : 0) | None | 22.8 | 0 | 0 | 0 | 6.0 | 0 | 2 | 6.2 |
| | | | 3 | 0 | > 100 | 3.4 | 0 | > 100 | 5.5 |
| | | | 6 | 0 | > 100 | 3.6 | 0 | > 100 | 5.2 |
| " " (4 : 1) | None | 25.2 | 0 | 0 | 0 | 5.2 | 0 | 2 | 6.0 |
| | | | 3 | 0 | > 100 | 2.8 | 0 | > 100 | 7.0 |
| | | | 6 | — | — | — | 0 | > 100 | 5.5 |
| " " (1 : 1) | None | 24.9 | 0 | 0 | 0 | 5.1 | 0 | 2 | 5.7 |
| | | | 3 | 0 | 63 | 3.9 | 0 | > 100 | 6.5 |
| | | | 6 | 0 | > 100 | 3.4 | 0 | > 100 | 6.5 |
| " " (1 : 3) | None | 26.0 | 0 | 2 | 0 | 5.5 | 0 | 3 | 6.4 |
| | | | 3 | 42 | > 100 | B.E.* | 0 | > 100 | 7.2 |
| | | | 6 | 11 | > 100 | B.E. | 0 | > 100 | 7.0 |
| " " (1 : 0) | Zinc Borate | 27.9 | 0 | 0 | 3 | 4.5 | 0 | 4 | 4.5 |
| | | | 3 | 0 | 48 | 3.7 | 0 | 43 | 4.5 |
| | | | 6 | 0 | 81 | 3.4 | 0 | 103 | 4.7 |
| " " (4 : 1) | Zinc Borate | 27.8 | 0 | 0 | 2 | 4.4 | 0 | 3 | 4.7 |
| | | | 3 | 0 | > 100 | 3.1 | 0 | 61 | 4.5 |
| | | | 6 | — | — | — | 0 | > 100 | 5.0 |
| " " (1 : 1) | Zinc Borate | 37.6 | 0 | 0 | 0 | 4.4 | 0 | 2 | 4.5 |
| | | | 3 | 0 | 15 | 4.6 | 0 | 53 | 4.7 |
| | | | 6 | 0 | > 100 | 4.2 | 0 | > 100 | 5.4 |

Table 38. Substitution of 40% Chlorinated Paraffin and 70% Chlorinated Paraffin for Vinylite VYNS in the Antimony Oxide-Vinylite Solvent Suspension Treatment (*Continued*)

| Vinylite : Chlorinated Paraffin Ratio | Glow Retardant | Total Add-On % | No. of Launderings in 0.5% G.I. Soap | 45°-Microburner Flame Test | | | Vertical-Bunsen Flame Test | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Afterflame sec. | Afterglow sec. | Char Area in² | Afterflame sec. | Afterglow sec. | Char Length in. |
| | | | 0 | 43 | 0 | B.E.* | 45 | 0 | B.E. |
| VYNS : 40% C.P. (1 : 3) | Zinc Borate | 27.0 | 3 | 22 | > 100 | B.E. | 0 | > 100 | 5.7 |
| | | | 6 | 15 | > 100 | B.E. | 0 | > 100 | 5.7 |
| | | | 0 | 0 | 0 | 6.0 | 0 | 2 | 6.2 |
| " " (1 : 0) | None | 22.7 | 3 | 0 | > 100 | 3.4 | 0 | > 100 | 5.5 |
| | | | 6 | 0 | > 100 | 3.6 | 0 | > 100 | 5.2 |
| | | | 0 | 0 | 0 | 4.7 | 0 | 2 | 5.0 |
| " " (3 : 1) | None | 25.3 | 3 | 0 | > 100 | 4.3 | 0 | > 100 | 5.0 |
| | | | 6 | 0 | > 100 | 2.8 | 0 | > 100 | 6.1 |
| | | | 0 | 0 | 2 | 4.6 | 0 | 2 | — |
| " " (1 : 1) | None | 30.7 | 3 | 0 | 21 | 5.2 | 0 | 96 | — |
| | | | 6 | 0 | > 100 | — | 0 | > 100 | — |
| | | | 0 | 0 | 3 | 4.5 | 0 | 4 | 4.5 |
| " " (1 : 0) | Zinc Borate | 27.9 | 3 | 0 | 48 | 3.7 | 0 | 43 | 4.5 |
| | | | 6 | 0 | 81 | 3.4 | 0 | 103 | 4.7 |
| | | | 0 | 0 | 0 | 4.3 | 0 | 4 | 5.0 |
| " " (3 : 1) | Zinc Borate | 28.2 | 3 | 0 | 108 | 2.8 | 0 | 64 | 4.5 |
| | | | 6 | 0 | > 100 | 3.3 | 0 | > 100 | 4.7 |
| | | | 0 | 0 | 0 | 3.6 | 0 | 3 | 4.0 |
| " " (1 : 1) | Zinc Borate | 33.5 | 3 | 0 | 3 | 4.0 | 0 | 36 | 3.5 |
| | | | 6 | 0 | > 100 | 3.0 | 0 | 60 | 3.5 |

* B.E. — Burned to the end.

obtained compared to that of the other types of durable treatments. The results of the evaluation tests on this treated fabric will be presented in the following chapter.

### (c) *Solvent Suspensions*

Since the antimony oxide-chlorinated resin type of flameproofing mixture had been previously used by the Chemical Warfare Service Laboratories at the Massachusetts Institute of Technology [25] and also in the tentage program of the Quartermaster Corps in the form of a solvent suspension, an attempt was made to apply the glowproofed combination developed above in the suspension form. It was felt that comparable glow-resistant properties could be incorporated into that treatment and that the method of application might produce a greater degree of permanence than was achieved with the emulsion. The general formula for the solvent suspensions prepared was as follows:

| | |
|---|---|
| Copolymer vinyl chloride-acetate (Vinylite VYNS) | 8.8 parts |
| Antimony oxide | 8.8 " |
| Zinc borate | 2.9 " |
| Triphenyl phosphate | 8.8 " |
| Methyl ethyl ketone | 70.7 " |

Investigations of the effectiveness of this treatment on 8.5 oz. herringbone twill led to the decision that, as in the case of the emulsion, the minimum effective add-on was approximately 30%. Adequate flame retardancy was achieved with additions of approximately 27% but the resistance to afterglow was much better, both initially and after laundering, with add-ons slightly above 30%.

**Variations of Chlorinated Body.** With the intention of improving the objectionable hand of the fabric treated with the Vinylite mixture, suspensions were prepared in which the resin was partially or wholly replaced by 40% or 70% chlorinated paraffin. Half of the preparations in this series contained zinc borate while the remainder did not possess any added glow retardant. The results of these investigations, as summarized in Table 38, verified the findings of the emulsion experiments as to the relative efficiencies of the different chlorinated products in preventing afterflaming. The order of effectiveness of the three materials employed was 70% chlorinated paraffin > Vinylite VYNS > 40% chlorinated paraffin which was shown earlier to be in the same order as the relative amounts of available hydrochloric acid and the ease with which it was liberated at combustion temperatures. The formulations which included zinc borate were noticeably superior in their glow-resistant properties to those which

[25] M.I.T.—M.R. No. 45—Memorandum Report, "Fireproofing of Fabrics"—George Cohen, 1st Lt., C.W.S. (Sept. 24, 1944).

contained no added glow-retarding ingredient, particularly with respect to the permanence of the treatment. As far as the hand of the finished fabric was concerned, the mixtures containing greater amounts of 40% chlorinated paraffin were more satisfactory from that standpoint but exhibited less effective flameproofness. The use of the 70% wax did improve the flameproof characteristics but the hand of the fabric in this case was no better than with Vinylite alone. The add-ons obtained in this series of experiments were somewhat lower than the 30% desired. For this reason the data do not represent the maximum efficiency of these treatments but is felt to be satisfactory for drawing comparisons between the different mixtures.

As indicated in Table 38, the glow retardancy obtained with these solvent suspension treatments is fairly good but is impaired by standard laundering procedures. In order to investigate the relationship between the degree of polymerization of the resin and its covering and binding properties, a series of treatments were carried out in which Vinylite VYNS was replaced by similar copolymers of both higher and lower average molecular weights. The results of these experiments are presented in Table 39,

Table 39. Substitution of Vinylites VYHH and VYNL for VYNS in the Antimony Oxide-Vinylite Solvent Suspension Treatment

| Resin | No. of Launderings in 0.5% G.I. Soap | Add-On % | Afterflame sec. | Afterglow sec. | Char Area, in.² or Char Length, in. |
|---|---|---|---|---|---|
| | | *(45°-Microburner Flame Test)* | | | |
| VYHH | 0 | 29.6 | 0 | 0 | 2.9 |
| VYNS | 0 | 26.4 | 0 | 3 | 4.5 |
| VYNL | 0 | 27.3 | 0 | 2 | 2.9 |
| VYHH | 3 | 29.6 | 0 | 3 | 2.7 |
| VYNS | 3 | 26.4 | 0 | 48 | 3.7 |
| VYNL | 3 | 27.3 | 0 | 0 | 3.5 |
| VYHH | 6 | 29.6 | 0 | 130 | 3.3 |
| VYNS | 6 | 26.4 | 0 | 63 | 3.7 |
| VYNL | 6 | 27.3 | 2 | 0 | 3.4 |
| | | *(Vertical-Bunsen Flame Test)* | | | |
| VYHH | 0 | 30.2 | 0 | 2 | 4.5 |
| VYNS | 0 | 27.9 | 0 | 4 | 4.5 |
| VYNL | 0 | 29.3 | 0 | 3 | 4.5 |
| VYHH | 3 | 30.2 | 0 | 70 | 4.0 |
| VYNS | 3 | 27.9 | 0 | 43 | 4.5 |
| VYNL | 3 | 29.3 | 0 | 45 | 4.7 |
| VYHH | 6 | 30.2 | 0 | 158 | 4.5 |
| VYNS | 6 | 27.9 | 0 | 103 | 4.7 |
| VYNL | 6 | 29.3 | 0 | 108 | 5.0 |

Vinylite VYHH being of lower molecular weight than VYNS. There is no striking difference in the performance of the three resins in this particular

mixture although the tougher film of VYNL does exhibit a significant improvement in the retention of zinc borate on laundering. From a practical standpoint, however, the improvement in the permanence of the glow resistance is counterbalanced by the unfavorable solubility of the high molecular weight resin and the extremely stiff finish of the treated fabric.

**Most Satisfactory Formulation.** As in the case of the emulsion treatment, a preferred formulation was selected on the basis of the experiments just described and a larger yardage of fabric processed by small-scale commercial techniques. The mixture employed for this application was identical with that given above with the exception that, for safety reasons, methyl ethyl ketone was replaced by isophorone. In this case also the efficiency and permanence of the glow retardancy obtained were somewhat inferior to that experienced in the laboratory applications using the former solvent. Test data evaluating this treated fabric comparatively with the other durable type treatments are also presented in the following chapter.

## c. Industrial Processing

### *(1) Solvent Suspension*

*C. H. Masland, 2nd and Eugene B. McBride*

#### *(a) Processing of 242 Finish by Impregnation* *

Up to the present time, experience in the commercial application of the pigment-type flameproofing processes in the form of a solvent suspension has been limited primarily to the tentage finish as described in Tentative Specification J.Q.D. 242, December 2, 1942. The fabric thus impregnated is designated as "Duck, Cotton; Fire, Water and Weather Resistant."

During the war considerable yardage of cotton duck was processed with this finish employing both the immersion and roller and knife methods of application with equal success. This discussion will deal only with the immersion or "impregnation" method.

In preparing the impregnating compound, a paste is ground using principally the color pigments and a portion of the chlorinated paraffin. A second paste is prepared incorporating the antimony oxide and inhibitors. The two pastes are thoroughly mixed and then the additional resin solution and the remainder of the chlorinated paraffin are added. Finally, sufficient solvent is added to produce a compound having a total solids content of 80% by weight. This mixture is taken from storage as required and diluted for use in a large mixing tank. The compound is then fed from

* Contributed by Eugene B. McBride.

the mixer directly into the impregnating tank by gravity-flow through a heated pipe line.

The details of the application process are shown diagrammatically in Figure 16. The cloth is first heated on copper dry cans, fed by the conventional methods of either laminating the sewed rolls or by the use of scray. The predrying of the grey duck drives out most of the moisture rendering the fabric more absorbent. The fabric passes through a tension device into the V-shaped impregnation tank. The contents of the tank are continually mixed by means of a screw-type agitator in the bottom having a right and left thread so as to produce a circular motion of the compound.

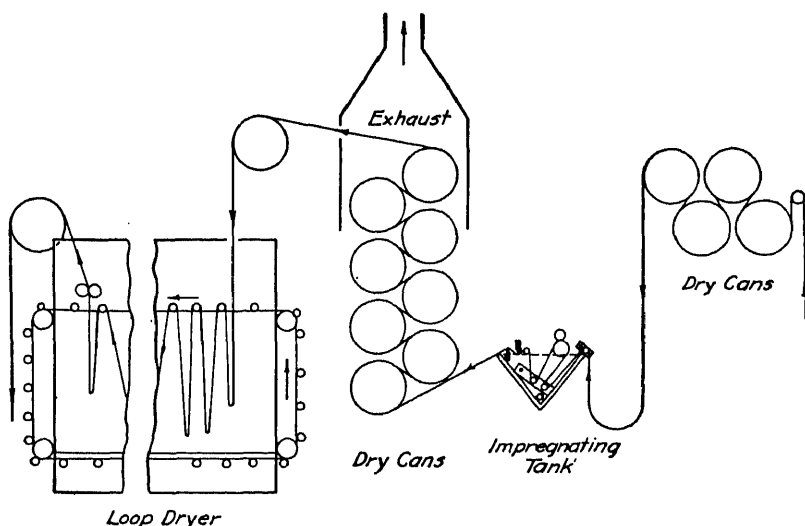



Figure 16. Commercial installation for the processing of fabrics by impregnation.

The tank is steam-jacketed and regulated to maintain a compound temperature of 110 ± 5° F. As shown in Figure 16, the fabric is deeply immersed into the compound, passes through a set of steel squeeze rolls followed by a second immersion. After the second dip the cloth proceeds through a set of doctor blades to the dryers.

It is worthwhile to note that the three bars in the tank, around which the fabric passes, do not rotate. They are held stationary to aid in penetration by producing an additional rubbing action which tends to force the compound into the fabric. The steel squeeze rolls are hollow having a diameter of 8 inches and are operated at a total pressure of 2000 pounds by means of the conventional lever system. The doctor blades consist of angle irons to which are clamped 2-inch strips of 0.020-inch hardened steel. This clamping arrangement permits new strips of material to be inserted quickly and easily.

In the drying stage of the process the fabric passes around a bank of vertical copper dry cans and then into a loop dryer. Sufficient drying is obtained on the cans to prevent marking of the finish by the sticks in the loop dryer. The latter is 30 feet long and contains four large fans for air circulation and an exhaust blower which produces six complete changes of air per minute. Approximately 250 yards of fabric are in the loop dryer at one time affording ample time for thorough drying at the operating temperature of $250 \pm 10°$ F.

On leaving the dryer, the cloth is laminated onto skids, allowed to cool in this position for at least one hour and finally packed into appropriate rolls for shipment.

In processing Army duck by this method the fabric runs at a speed of 25 yards per minute per strip using a suspension containing 60% solids. The installation is wide enough in this case to accommodate two strips of fabric of widths up to 36 inches.

The finishing process described in the preceding pages has been employed in finishing several million yards of cotton duck to meet the requirements of Tentative Specification J.Q.D. 242. The four factors involved which assist in obtaining better penetration are:

1. Reduction of the moisture content of the grey goods to a minimum.
2. Maintenance of the treating compound at the proper uniform temperature.
3. Use of squeeze rolls to force the compound into the fabric.
4. Use of rubbing bars.

The doctor blades are used after the squeezing and rubbing operations in order to prevent squeeze roll marks and produce a smooth, clean surface.

Many variations of the above process have been employed. While squeeze rolls and doctor blades are frequently used in series as shown, they may be used separately. The elimination of either one, however, may prevent the successful running of hard texture, heavy fabrics. Considerable variation may be made in the drying equipment without any effect on the finished fabric. Copper dry cans may be used exclusively but the danger of baking the finish if too many cans are employed should be kept in mind. The cloth may be led into vertical drying towers in which it passes over steel rolls located at the top and bottom of the tower. If the fabric is pulled by a card cloth roll at the output end of the dryer, the inside steel rollers may be run slightly faster, thus keeping the rolls clean and preventing printing of the finish.

The immersion technique described has been employed in processing tentage fabrics of several weights and weaves, ranging from hard texture, heavy duck, to tent twill, without any mechanical or technical difficulties.

### (b) *Processing of 242 Finish with Roller and Knife* *

In addition to the foregoing immersion method, cotton duck was also treated to conform to J.Q.D. 242 Specifications by applying the pigment-chlorinated paraffin-resin-solvent suspension by means of a knife or doctor blade. The three principal variations of this general process will be considered in this discussion.

In the first method, shown diagrammatically in Figure 17, the fabric is impregnated on one side only. After complete drying the fabric is turned

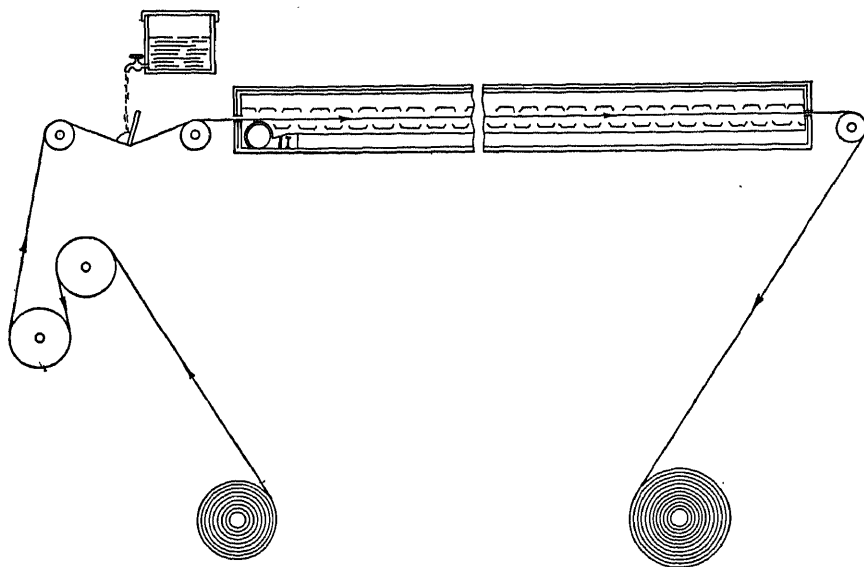



Figure 17. Commercial installation for knife-coating fabrics on one side only.

and re-run in order to impregnate the other side. The cloth first passes underneath a knife, the treating compound being run onto the fabric so as to form a pool ahead of the blade. The fabric then proceeds into a ventilated drier where volatile solvents are removed. In this simplest case, dependence is placed upon the pressure between the doctor blade or knife and the cloth to cause penetration of the compound into the interstices of the fabric.

In a second variation of this knife-coating process, the fabric is impregnated on both sides in one continuous operation, as illustrated in Figure 18. The cloth passes under a knife maintaining a pool of compound on the fabric ahead of the blade, and is then turned around a roller system and similarly impregnated on the other side of the fabric. In this case, the

* Contributed by C. H. Masland, 2nd.

treated material is dried on cylinders rather than in a ventilated hot-air dryer. The compound is usually prepared with a lower solvent content than in the case of the first method described. Penetration of the mixture into the fabric is secured not only by the pressure of the knives upon the cloth but also by the use of higher temperatures in the drying process. By raising the temperature of the cloth above the melting point of the compound while in contact with the drying cans better impregnation can be attained.

In a third method, shown in Figure 19, the compound is held in a trough containing two feed rollers. The fabric passes over the upper surface of the feed rolls being held in tight contact by idler rollers. Having picked up the impregnating mixture from the feed rollers, the cloth passes over a knife which scrapes off excess compound and causes further compression into the fabric. In this case, impregnation is secured by a combination of the pressure of the cloth against the feed rolls and against the knife. After one side of the cloth has been processed it may be dried and re-run, or it may be turned around rollers and the other side similarly impregnated in one continuous operation prior to drying. In this third variation, employing roller and knife, the viscosity and solvent content of the mixture can be intermediate between those of the compounds employed in the first two techniques.

In all three methods of knife impregnation, uniformity of results depends upon several factors pertaining to the cloth, compound, knife and feed rollers. The cloth should be carefully controlled as to the tightness of weave, tension and flatness while being processed and uniformity of fabric temperature. The composition, viscosity, surface tension and temperature of the impregnating mixture must be maintained as nearly constant as possible. Finally, the pressure of the knife and feed rollers against the cloth must be held constant and attention must be given to the angle and sharpness of the knife and the arc of contact of the cloth with the applying rollers. The details of the methods of application discussed will of necessity vary from one plant to another. For that reason, one plant employing the third method above will be described in greater detail.

The treating compound was prepared in three stages. A rosin-modified phenol formaldehyde resin was crushed and then dissolved in an aromatic solvent in a steam-jacketed mixer at 30° C. Chlorinated paraffin was added to this varnish solution and agitated until dissolved. All pigments were formed into a slurry utilizing the remainder of the chlorinated paraffin and a small amount of solvent as the blending medium. Proper amounts of each of these two stock mixes were then pumped into weighing cans and combined in a final mixer. The final mix contained approximately 43% pigment, 57% resin and chlorinated paraffin and 28% solvent. Only the solvent used in dissolving the resin was aromatic, solvent added in the final mix and used in thinning the pigment slurry being a mixture of

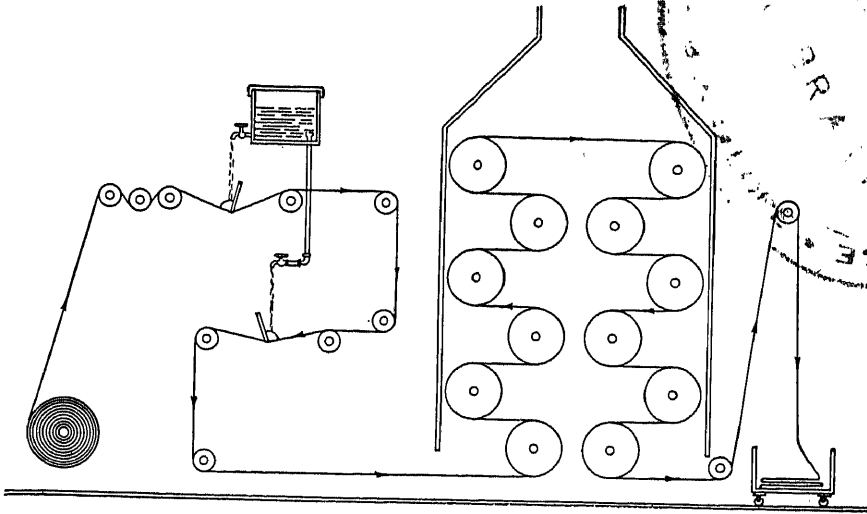
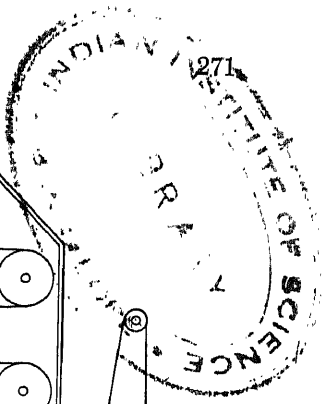



Figure 18. Commercial installation for the knife-coating of fabrics; continuous range for impregnating both sides of the fabric.

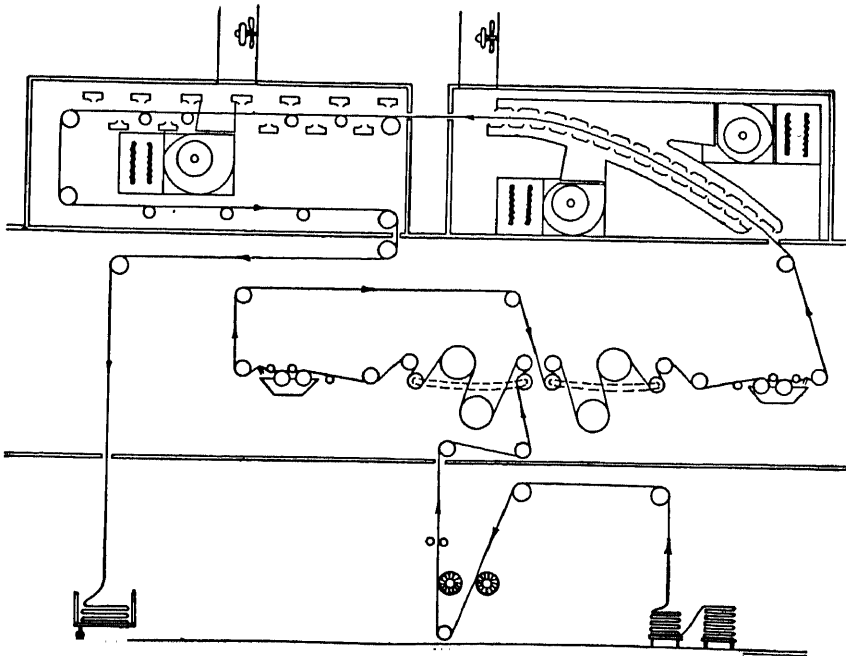



Figure 19. Commercial installation for the continuous two-side impregnation of fabrics by roller and knife.

Stoddard Solvent and V.M.P. Naphtha. After completing the final m
samples were tested for viscosity and surface tension. The compound w
then pumped from the final mixing tank to the application trough in
closed circuit. The pipes leading to and from the application trough we
enclosed in an insulated box along with a steam pipe permitting regul
tion of the temperature of the compound being delivered. The mixture
the treating trough was agitated by withdrawing from the bottom of t
trough and returning to the bath by pumping through distributing nozz
along the side at surface level. The suspension was circulated in tl
manner in order to insure uniformity of composition and also to mainta
constant temperature at the point of application.

The grey cloth was lapped onto trucks from rolls as received, sewn en
less and passed between brushes and suction nozzles to remove fibers a
loose particles. Controlled by an automatic guider, the fabric was th
passed over steam-heated cylinders which were driven at a different
speed to develop a tension in the cloth. The cylinders or dry cans we
regulated for a fabric temperature of 110° F. which was found to aid
securing penetration of the heavier number ducks. The tension of the clo
on and between the hot cylinders caused it to conform to the cylindric
surface and at the same time assisted in stretching out slack places
the cloth. It will be noted that the tension developed was not carried ov
into the dryer since it was caused only by the differential in the speeds
the two cylinders. The tension of the cloth passing over the knife and in
the dryer was controlled separately.

The knives used were 28-gage steel blades backed up by strips
heavier 18-gage steel. These were adjusted, as shown in Figure 20, wi
the end of the heavier strip 5/16 of an inch below the upper edge of t
28-gage blade. This system provided the desired flexibility so that t
knife could follow irregularities in the cloth and yet retained sufficie
stiffness to produce pressure.

As shown in Figure 19, the fabric passed from one impregnation unit
the next permitting continuous processing of both sides of the cloth. Fro
the second trough the cloth was led directly into the dryer. In the fi
dryer, air at 185° F. was blown against both sides of the fabric at hi
velocity and circulated throughout by means of a fan and heater syste
The cloth proceeded on into a second dryer in which it was again su
jected to high velocity hot air, this time at 175° F., similarly circulat
through a heater and fan system. Exhaust fans were installed in bo
dryers and sufficient solvent vapors were removed and fresh air introduc
to restrict the solvent content of the air in the dryer to less than 70%
the lower explosive limit of that particular solvent-air mixture. Followi
drying, the finished fabric was measured and rolled ready for warehousi

**Safety Precautions.** Although the safety measures needed will va
from plant to plant, certain points may be mentioned as being of possil

general interest. All solvents were held in underground storage tanks and pumped by motor-driven pumps directly to the mixing tanks. The pump motors were controlled by push buttons at each mixing tank and it was necessary for the operator to stand at the tank with his finger on the control button while the tank was being filled. All mixing tanks were vented to the outside atmosphere. They were also thoroughly grounded, and all driving belts both for mixers and dryer fans were equipped with static removers. All mixing tanks were equipped with automatic $CO_2$ extinguishers with outlets under the lid of the tank. Motors were set more than six feet above the working floor. All switches were safety switches of the enclosed vapor-proof type as was also the case with all lighting fixtures.

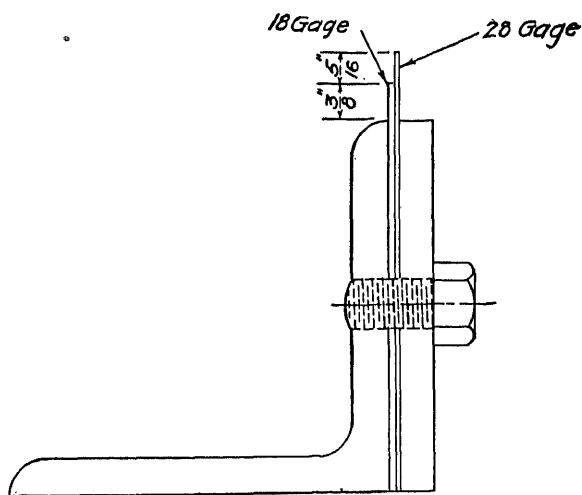



Figure 20. Diagram of knife or "doctor-blade" employed in the knife-coating of fabrics.

The coating troughs were housed in separate enclosures, each enclosure having its own exhaust system. Also each enclosure was capable of being flooded with $CO_2$ from nozzles both directly over the impregnating troughs and throughout the enclosure. These $CO_2$ nozzles were controlled by rate-of-temperature-rise controllers placed over the impregnating troughs in each enclosure. In all cases, the $CO_2$ could also be released manually.

The dryers were protected by automatic sprinklers and open steam nozzles capable of being manually operated in case of fire. The first dryer in which the greatest amount of solvent was evaporated was protected by an Explosimeter which continually drew samples of the atmosphere from within the dryer and analyzed them for solvent content. The second dryer was similarly equipped. All exhaust fans and the two Explosimeters were connected electrically with the driving mechanism of the installation so that a failure of a fan or an increase in the solvent content of the dryers above 70% of the lower explosive limit would shut down the whole range.

In addition to the stationary explosimeters a portable model was used

to test the atmosphere at 15 danger points during each shift. All hand tools, such as wrenches or chisels, were made of beryllium copper in order to avoid the hazard of sparks.

Although only a relatively small portion of aromatic solvents was used in the compound and each tank was individually vented to the atmosphere, it was considered desirable to check each individual working in that department to determine whether his health was being affected by the inhalation of toxic aromatic solvents. For that purpose, a blood count was made of each workman at regular intervals. A decrease in the red cell count is indicative of possible cumulative effects of breathing benzol or toluol.

Doubtless many improvements in method will be made but the foregoing processes gave satisfactory results as to quality and safety during the war.

### *(2) Emulsion*

*Joseph R. Morton*

As has been previously mentioned, practically all treatments for the flameproofing of textiles by the metallic oxide-chlorinated body type of process had been done, prior to our entry into World War II, from solvent suspensions. These suspensions were generally applied with knife coating equipment similar to that used for pyroxylin coatings. This method of application was slow, and in many instances the cloth was subjected to two runs, coating one side at a time. This procedure was gradually replaced by a single immersion where two knives or doctor blades were used to scrape the excess from each side.

The types of compounds used for such processes consisted primarily of mixtures of chlorinated rubber, chlorinated paraffin, borates, resins, color pigments and solvent.

Treatments applied in the above manner presented difficulties as regards processing, fabrication, and later service under the conditions for which they were used. At best, the application to the fabric was quite slow and costly, and, in addition, presented serious hazards because of the inflammable nature of the solvents employed. The treated cloth was usually dried at temperatures considerably above the flash points of these solvents, and to this one hazard alone can be attributed a number of fires and explosions resulting in both loss of life and property damage.

In addition, the finished cloth was in many instances very difficult to handle during the fabrication operations. Some of it was sticky, crocked badly, and was not in good condition for cutting and sewing. Trouble was also experienced during fabrication from solvent fumes from the treated cloth, frequently caused by imperfect drying. Another deficiency was lack of sufficient flexibility.

It was subsequently found that the borates and zinc compounds contributed to the rapid decomposition of the chlorinated bodies, thereby causing tendering of the finished cloth, particularly under certain weathering conditions. The wide use of antimony oxide, which began several years ago, made possible considerable improvements in this respect.

Finally, the use of this solvent method of application suffered because of a lack of uniformity. At times, the compound used in the process failed to achieve proper penetration and because of this it was sometimes necessary to apply abnormally high amounts to the fabric in order to meet certain portions of the specifications, particularly those pertaining to flame and char. Other processors found that with this type of compound, under solvent phase knife coating application, it was impossible to reduce the add-on below approximately 60% even though lower add-on might have produced satisfactory tests. Such a procedure was objectionable, not only because of cost, but because of added weight and decreased flexibility.

### (a) *Development of Emulsion*

Believing that there was a definite relationship between the viscosity of the compound, the concentration of active ingredients and the dry add-on that would be obtained on the cloth, work was initiated to discover the effects of this relationship, and, if possible, therefrom to improve the methods of application. It was felt that if a given concentration of active ingredients could be maintained and the viscosity varied that the desired control of add-on could be achieved. It being impossible to obtain this type of result from straight solvent solution, it was decided to try an emulsion phase coating and search was instituted for an emulsifier that would possess sufficient power and stability to permit of the variations in viscosity that were desired. One such agent was developed that made it possible when used to the extent of 0.5% in conjunction with 2.0% solvent naphtha and a small amount of zinc chloride to tolerate 97% water and, under rapid agitation, produce an emulsion that was very thick and extremely stable. This emulsion exhibited, among other desirable qualities, that of variable viscosities, it being possible to reduce this by the addition of more solvent or to increase it by the addition of water. Excellent stability was obtained under both conditions.

The development of this variable viscosity type of emulsion in the flameproofing compound provided a yardstick by which add-on could be controlled through variations of the solids-viscosity ratio. This was an extremely important development as it meant that practically any desired add-on could be obtained and that this could be held within closer limits under varied and changeable manufacturing conditions than had been possible with the solvent method of application.

The emulsions produced in this work and generally used later in full-

scale production were primarily of the water-in-oil type. Not only was a way provided for controlling add-on, but it was observed that other interesting characteristics were obtained. Notably, this improvement related to greater penetration, it being found that thorough dispersion of the treating materials was obtained throughout the fibers of the cloth. This naturally resulted in the achievement of a more uniform degree of flame, char and mildew resistance within the allowable add-on limits.

With these indications from the early development work, production scale tests were then begun using these water-in-oil emulsion types with variations in total solids of 40, 45 and 55% respectively. At each of these concentrations varying ratios of solvent and water were added. Stability tests were then made on a printing machine for a period of two hours, the roll being equipped with a doctor blade and set at a speed necessary to print 60 yards of cloth per minute. The results are shown in Table 40. Viscosities are expressed relative to the viscosity of water which is taken as unity.

Table 40. Comparison of Stability and Viscosity of Emulsions of Various Concentrations
(*Morton Chemical Company Prufduk 746-B*)

| Solids Content | Composition | | | Emulsion Stability | | Emulsion Viscosity (water = 1) | |
|---|---|---|---|---|---|---|---|
| | Prufduk | Solvent | Water | Before | After | Before | After |
| 40% | 100 | 52 | 85.5 | Stable | Stable | 9.1 | 12.2 |
| | 100 | 45.5 | 92 | " | " | 13.4 | 22.9 |
| | 100 | 18 | 119.5 | " | Slight $H_2O$ break | 722.5 | 586.4 |
| 45% | 100 | 44 | 67 | Stable | Stable | 9.7 | 14.3 |
| | 100 | 34 | 77 | " | " | 25.5 | 51.4 |
| | 100 | 16 | 95 | " | " | 228.9 | 485.0 |
| 55% | 100 | 27.5 | 45 | Stable | Stable | 13.8 | 19.5 |
| | 100 | 21.5 | 51 | " | " | 62.8 | 120.4 |
| | 100 | 7 | 65.5 | " | " | 3023.3 | 3045 |

It will be noticed from an examination of the above table that in the case of the 55% solids concentration, the viscosity varied from 13.79 to 3023.3, and that stability was obtained at each of these extremes. In general, there were slight increases in the viscosities after running for two hours, and in one instance, a slight break occurred in the emulsion, resulting in a lowering of the viscosity. This was probably caused by the evaporation of solvent during the run. This condition would not be encountered in normal plant production since under such conditions, the supply of emulsion would be continually replenished.

After thorough investigation, it was found that the best method for preparing the emulsion was to begin by making a preliminary solution consisting of all the active ingredients with a minimum quantity of solvent. This extremely heavy solution was then diluted with the remainder

of the solvent, after which the water was added. With good agitation, the water portion could be added rapidly. Emulsions made in this manner retained their stability almost indefinitely, there being but a slight increase in viscosity upon long standing. In such cases, the original viscosity could be regained with slight additional agitation.

The next stage of the development was to test these emulsions under commercial application conditions. A textile padder was chosen which would permit of variation in the squeeze and at the same time maintain a very rapid application. With this it was found possible to obtain uniformly good penetration at high application speeds.

The resulting treated fabrics possessed some interesting and significant properties. The improved penetration gave them more of the appearance of a dyed finish in contrast to many solvent type applications. When these treated fabrics resulting from the emulsion runs were pulled apart, no white, untreated spots were observed, this being a further indication of greatly improved penetration. Several series of tests have been made using exactly the same active compound ingredients in both water-in-oil emulsions and ordinary solvent suspensions. The emulsion technique was found to be consistently superior to the solvent method with respect to penetration and uniformity.

Further testing showed that both flameproofing and waterproofing qualities were improved. The emulsion-treated fabrics exhibited shorter char lengths and better hydrostatic properties than were shown by the solvent suspension treated goods used for comparison. In all the other tests, the emulsion-treated fabrics performed well. Finally, because of the increased penetration, it was possible to reduce somewhat the unit quantities of active ingredients required, and still completely meet specification performance requirements. This resulted in a saving of some critical materials in addition to a lower cost.

### (b) *Industrial Application*

Although the water-in-oil technique was preferred for most fabrics, there were some applications where oil-in-water type emulsions were considered superior. This latter type of emulsion did not result in as good penetration as previously described but it did deposit more material on the surface, and hence imparted a more intense color to the finished fabric. This was an important consideration with such materials as camouflage shrimp netting and the Osnaburg or burlap camouflage strips. These materials were of such a loose weave that penetration was easy to obtain and therefore the oil-in-water emulsion type could be employed.

An important factor affecting the emulsion treatments is that they lend themselves to running on a wide variety of application equipment. Probably the most desirable type of equipment for handling most fabrics is a

textile padder equipped with rolls of equal density and with both rolls positively driven. It is recommended in application on this type of equipment that the goods be given a thorough immersion in the pad box to a depth of six to eight inches, after which they are passed through the squeeze rolls where the excess compound is removed. While this method of application is favored it has been found that excellent results can be obtained with other types of equipment. Knife coaters, where the coating compound is delivered by a fountain or where the goods are immersed and then pulled between two scrapers, have been used quite satisfactorily. It has also been found possible to use a machine, such as a textile printing machine, where the emulsion is taken up by a roller and deposited on the surface of the cloth. In none of these latter types, however, is quite the degree of penetration or uniformity obtained as with the padder, and if a knife coater is used it is recommended that a set of squeeze rolls be installed following the knives as this not only promotes levelness but eliminates the difficulty that is so often encountered in knife coating through excessive compound collecting on the selvages.

Various forms of drying equipment have been used successfully. The best results, however, have been found to obtain when some form of surface dryer is used immediately following the application, such as a heated and ventilated tenter frame or other hot air dryer. Once the surface moisture is removed the goods can be put on to dry cans, or any other available form of dryer, and the drying completed. Goods treated with the water-in-oil type of emulsion usually dry quite easily as the water from the emulsion is left free on the surface after application from whence it is easily removed and there is then a much smaller quantity of solvent to be extracted from the fibers than is the case with the usual solvent type treatment.

These emulsion treatments show a ready adaptability for many types and weights of fabrics. This adaptability has made possible significant and large-scale commercial application. In most instances it has been found that by merely changing the viscosity of the treating emulsion it could be adapted to give the desired results on a variety of fabrics. A soft twisted, open construction fabric is best treated with an emulsion of high viscosity, while to get the desired penetration on a hard twisted, tightly woven duck it is usually necessary to use a considerably lower viscosity. As experience is built up by the coater he can usually estimate and control his add-on very readily by varying the viscosity of his emulsion.

In addition to the previously cited advantages of the emulsion treatment, there are several others of importance. These include freedom from tack, dryness of finish, increased flexibility and greatly improved resistance to crocking. These are all of considerable importance for both military and civilian use.

### (c) *Formulation and Effect of Various Compounds*

**Oil-in-Water Emulsions.** This type of emulsion will require higher percentages of active ingredients than the water-in-oil type since the treatment is essentially a surface effect. Emulsification agents commonly used include the sodium, potassium, and ammonium salts of various fatty acids, as well as the sulfonated alcohols. For this type emulsion it is, of course, necessary to use a water-soluble emulsifier.

**Water-in-Oil Emulsions.** In preparing this class of products, it is necessary to select an emulsifying agent which is soluble in the particular organic solvent to be employed, it, of course, being desirable to have one with as wide a degree of organic solubility as possible. These emulsifiers are mostly complex organic compounds, some of them falling within the classes of esters and amino condensates. A typical formulation for a water-in-oil type emulsion compound for the treatment of plied yarn cotton duck is as follows:

| | |
|---|---|
| Chlorinated paraffin 42% | 19.0 |
| Chlorinated paraffin 70% | 12.0 |
| Resins | 16.25 |
| Copper and Copper hydroxy Naphthenate compound (11% Cu) | 9.5 |
| Antimony oxide | 13.75 |
| Calcium carbonate | 16.0 |
| Color | 8.4 |
| Solvent | 5.0 |
| Emulsifier | .7 |

To prepare the treating emulsion from the above compound a 60% solids emulsion might be prepared by dispersing 100 pounds of the compound in 25 pounds of naphtha and then adding 35 pounds of water under rapid agitation. It has been found that this produces an emulsion of approximately the right solids content and viscosity to produce approximately 50% dry pickup on 12.29 duck.

The amended Navy Specification 27–D–1 called for an afterglow time of three minutes or less on 2.50 life jacket drill. It was found that this could be accomplished with the addition of a small amount of zinc oxide to the regular formula.

**Use of Plasticizers.** Plasticizers which are commonly used in flame-resistant fabric coatings such as have been previously described include tricresyl phosphate, triphenyl phosphate, and dibutyl sebacate. Their effect upon water repellancy and the ultimate water resistance of the finishing system should be closely watched, since rather large differences may occur. The excessive use of some of them has been observed in some tests to completely destroy the water repellancy of certain treatments.

Table 41. Effect of Leaching and Accelerated Aging Tests Upon the Flameproofness, Strength, and Water Permeability of Emulsion-Treated Fabrics

| Navy Life Jacket Cover Compound | Fabric | Add-On % | Treatment of Fabric Prior to Testing | Cut of Specimens | Flameproofness (Vertical-Bunsen Test) After-flame sec. | After-glow sec. | Char Length in. | Breaking Strength (grab) Tensile Strength lbs./in. | % Change * | Water Permeability (Hydrostatic leakage test) cc. |
|---|---|---|---|---|---|---|---|---|---|---|
| #1 | 2.50 drill | 0 | Untreated grey goods | warp | — | — | — | 140.6 | — | — |
| | | | | filling | — | — | — | 71.0 | — | — |
| | | | Grey goods after 200 hours accelerated weathering | warp | — | — | — | 112.3 | – 19.9 | — |
| | | | | filling | — | — | — | 84.0 | + 15.4 | — |
| | | 62.5 | Treated fabric | warp | 0 | 75 | 2.9 | 174.8 | + 24.3 | — |
| | | | | filling | 0 | 72 | 2.9 | 109.3 | + 53.9 | — |
| | | | Treated fabric after 200 hours accelerated weathering | warp | 0 | 44 | 2.1 | — | — | — |
| | | | | filling | 0 | 57 | 2.2 | — | — | — |
| | | | Treated fabric oven-aged 3 days at 158° F | warp | — | — | — | 197.5 | + 40.4 | — |
| | | | | filling | — | — | — | 140.0 | + 97.1 | — |
| #2 | #12 duck | 0 | Untreated grey goods | warp | — | — | — | 175.2 | — | — |
| | | | | filling | — | — | — | 116.6 | — | — |
| | | 62.0 | Treated fabric | warp | 0 | — | 2.2 | 208.0 | + 18.7 | 1 |
| | | | | filling | 0 | — | 2.3 | 163.6 | + 40.3 | |
| | | | Treated fabric after 72 hours water leach ** | warp | 0 | — | 2.2 | — | — | 0 |
| | | | | filling | 0 | — | 1.5 | — | — | |
| | | | Treated fabric after 100 hours accelerated weathering *** | warp | 0 | — | 2.3 | — | — | 18 |
| | | | | filling | 0 | — | 3.2 | — | — | |
| | | | Treated fabric oven-aged 10 days at 180° F. | warp | — | — | — | 226.0 | + 28.9 | |
| | | | | filling | — | — | — | 209.6 | + 79.8 | |

Table 41. Effect of Leaching and Accelerated Aging Tests Upon the Flameproofness, Strength, and Water Permeability of Emulsion-Treated Fabrics (*Continued*)

| Navy Life Jacket Cover Compound | Fabric | Add-On % | Treatment of Fabric Prior to Testing | Cut of Specimens | Flameproofness (Vertical-Bunsen Test) After-flame sec. | After-glow sec. | Char Length in. | Breaking Strength (grab) Tensile Strength lbs./in. | % Change * | Water Permeability (Hydrostatic leakage test) cc. |
|---|---|---|---|---|---|---|---|---|---|---|
| #2 | #4 duck | 0 | Untreated grey goods | warp | — | — | — | 430 + | — | — |
| | | | | filling | — | — | — | 313.4 | — | |
| | | 42.4 | Treated fabric | warp | 0 | — | 0.2 | 430 + | — | 3 |
| | | | | filling | 0 | — | 0.4 | 350.6 | + 11.8 | |
| | | | Treated fabric after 72 hours water leach ** | warp | 0 | — | 0.2 | — | — | 0 |
| | | | | filling | 0 | — | 0.3 | — | — | |
| | | | Treated fabric after 100 hours accelerated weathering *** | warp | 0 | — | 0.4 | — | — | 0 |
| | | | | filling | 0 | — | 0.3 | — | — | |
| | | | Treated fabric oven-aged 10 days at 180° F | warp | — | — | — | 430 + | — | — |
| | | | | filling | — | — | — | 429 | + 37 | |
| | Army twill | 0 | Untreated grey goods | warp | — | — | — | 210.2 | — | — |
| | | | | filling | — | — | — | 141.0 | — | |
| | | 59.7 | Treated fabric | warp | 0 | — | 1.6 | 265.0 | + 26 | 0 |
| | | | | filling | 0 | — | 1.9 | 165.6 | + 16.9 | |
| | | | Treated fabric after 72 hours water leach ** | warp | 0 | — | 1.7 | — | — | 0 |
| | | | | filling | 0 | — | 1.7 | — | — | |
| | | | Treated fabric after 100 hours accelerated weathering *** | warp | 0 | — | 2.5 | — | — | 4 |
| | | | | filling | 0 | — | 2.0 | — | — | |

* % deviation from strength of untreated grey goods.
** Water changed every 24 hours.
*** No filters used.

(*Continued on next page*)

Table 41. Effect of Leaching and Accelerated Aging Tests Upon the Flameproofness, Strength, and Water Permeability of Emulsion-Treated Fabrics (*Continued*)

| Navy Life Jacket Cover Compound | Fabric | Add-On % | Treatment of Fabric Prior to Testing | Cut of Specimens | Flameproofness (Vertical-Bunsen Test) After-flame sec. | After-glow sec. | Char Length in. | Breaking Strength (grab) Tensile Strength lbs./in. | % Change * | Water Permeability (Hydrostatic leakage test) cc. |
|---|---|---|---|---|---|---|---|---|---|---|
| #2 | Army twill | | Treated fabric oven-aged 10 days at 180° F. | warp | — | — | — | 198.7 | − 5.7 | — |
| | | | | filling | — | — | — | 147.0 | + 3.8 | |
| #3 | #12 duck | 0 | Untreated grey goods | warp | — | — | — | 175.2 | — | — |
| | | | | filling | — | — | — | 116.6 | — | |
| | | 53.8 | Treated fabric | warp | 0 | — | 2.3 | 194.0 | + 10.7 | 8 |
| | | | | filling | 0 | — | 2.2 | 147.6 | + 26.6 | |
| | | | Treated fabric after 72 hours water leach ** | warp | 0 | — | 2.5 | — | — | 0 |
| | | | | filling | 0 | — | 2.3 | — | — | |
| | | | Treated fabric after 100 hours accelerated weathering *** | warp | 0 | — | 3.7 | — | — | — |
| | | | | filling | 0 | — | 3.2 | — | — | |
| | | | Treated fabric oven-aged 10 days at 180° F | warp | — | — | — | 167.3 | − 4.3 | — |
| | | | | filling | — | — | — | 140.3 | + 20.3 | |
| | # 4 duck | 0 | Untreated grey goods | warp | — | — | — | 430 + | — | — |
| | | | | filling | — | — | — | 313.4 | — | |
| | | 41.4 | Treated fabric | warp | 0 | — | 0.4 | 430 + | — | 0 |
| | | | | filling | 0 | — | 0.5 | 355.6 | + 13.4 | |
| | | | Treated fabric after 72 hours water leach ** | warp | 0 | — | 0.4 | — | — | 0 |
| | | | | filling | 0 | — | 0.4 | — | — | 0 |
| | | | Treated fabric after 100 hours accelerated weathering *** | warp | 0.5 | — | 0.7 | — | — | 6 |
| | | | | filling | 0 | — | 0.6 | — | — | |

Table 41. Effect of Leaching and Accelerated Aging Tests Upon the Flameproofness, Strength, and Water Permeability of Emulsion-Treated Fabrics (*Continued*)

| Navy Life Jacket Cover Compound | Fabric | Add-On % | Treatment of Fabric Prior to Testing | Cut of Specimens | Flameproofness (Vertical-Bunsen Test) After-flame sec. | After-glow sec. | Char Length in. | Breaking Strength (grab) Tensile Strength lbs./in. | % Change * | Water Permeability (Hydrostatic leakage test) cc. |
|---|---|---|---|---|---|---|---|---|---|---|
| #3 | #4 duck | | Treated fabric oven-aged 10 days at 180° F. | warp | — | — | — | 430 + | — | — |
| | | | | filling | — | — | — | 348 | + 11.0 | |
| | Army twill | 0 | Untreated grey goods | warp | — | — | — | 210.2 | — | — |
| | | | | filling | — | — | — | 141.6 | — | |
| | | 56.4 | Treated fabric | warp | 0 | — | 2.2 | 234.3 | + 11.4 | 1 |
| | | | | filling | 0 | — | 2.0 | 170.6 | + 20.4 | |
| | | | Treated fabric after 72 hours water leach ** | warp | 0 | — | 2.0 | — | — | 0 |
| | | | | filling | 0 | — | 2.0 | — | — | |
| | | | Treated fabric after 100 hours accelerated weathering *** | warp | 0 | — | 2.9 | — | — | 2 |
| | | | | filling | 0 | — | 2.3 | — | — | |
| | | | Treated fabric oven-aged 10 days at 180° F | warp | — | — | — | 188.6 | − 11.4 | — |
| | | | | filling | — | — | — | 165.6 | + 16.9 | |

* % deviation from strength of untreated grey goods.
** Water changed every 24 hours.
*** No filters used.

**Conclusions.** Briefly, it is felt that the emulsion treatment offers several distinctive advantages, such as:

1. Superiority of Finish—It has been demonstrated that through the penetration achieved with this type of coating greater pliability, crock resistance, dryness of finish, increased tensile strength, and greater levelness of shade may be obtained.

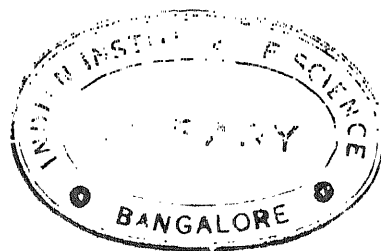
2. Ease of application and adaptability to a wide variety of application equipment, such as is found in most plants, coupled with the facility with which viscosity may be varied and thereby the add-on controlled.

3. Greater Safety—Since the use of water in the emulsion increases the flash point of the solvent at least 50° F. and thereby provides a much safer operation.

4. Saving in Cost—Since it has been found that due to the thorough permeation of the fibers, the desired results can be obtained with lower add-on than with the solvent method.

The table on the preceding pages gives some of the typical test data obtained by an examination of various emulsion coatings (Table 41).

# Section Three

## APPLICATIONS

## INTRODUCTORY

*E. Folger Taylor*

The experiences of World War II have shown that flame-resistant fabrics have numerous important uses within a military machine. Tarpaulins, tents, camouflage nets, life jackets and special clothing, which are generally made from combustible cellulosic material, have been variously treated to make them flame resistant. The chief purpose of the treatment is to prevent the ignition and free combustion of the item as a result of exposure to heat sources such as shell bursts, incendiary bullets, gun flashes, burning oil and gasoline, hot pipes of tent heaters, sparks, lanterns, candles and cigarettes. By flameproofing of tents and the like, danger of the spread of conflagration is reduced, and the average useful life of the item increased. By flameproofing clothing for special tasks or occupations, where fire is an extreme hazard, the possibility of accidental ignition and free combustion of clothing can be eliminated.

Although the problems involved in the flameproofing of equipment and clothing appear to have a common basis, a successful process for use on equipment is not necessarily applicable to clothing because of the differences in the characteristics other than flame resistance, which attend the end use. For instance, a tent or a tarpaulin can be given a treatment which may increase its weight by 50 to 80%, reduce its flexibility, and give it a harsh "hand." A suitable clothing treatment, however, must avoid changing those properties of fabrics which make a physiologically acceptable garment. This is true not only for military but also for civilian uses. Thus at the beginning of the war there were two distinct categories of flame-resistant treatments which had a background of practical commercial application.

One treatment, which consisted of a combination of particular metallic oxides with chlorinated organic compounds, was suitable for treating cotton ducks for tents and tarpaulins. The antimony oxide-chlorinated organic compound treatment was chosen for this purpose principally because it was durable. It could be made to retain its flame-resistant qualities for long periods of continuous exposure to various climates. The major disadvantages of this type of treatment are the high percentage add-on required, and the increased stiffness and weight which interfere with fabrication into end items and render fabrics so treated physiologically unsuitable for use in clothing.

The second treatment, comprising combinations of various water-soluble flameproofing salts, was suitable for treating cotton fabrics used for clothing and drapes. Under dry conditions, some water-soluble type treatments are particularly suited for clothing because add-ons of only 10–15% are required to give excellent flame resistance and there is little impairment of the qualities of the fabric which make it suitable as a garment. However, this type of treatment is not durable, being readily removed by profuse sweating, rain, wading through streams, and laundering and it is therefore unsuitable for general military use.

Early in 1944 the urea-phosphate type treatment came to the attention of the Quartermaster Corps as the result of examination of patent applications under the War Secrecy Act. This type of treatment holds considerable promise since it is durable, low in add-on, low in cost and leaves the garment with as fine a "hand" as the original fabric. On the other hand, the treated fabrics show a loss in tensile strength, the extent of which depends on the details of the application process and the accuracy of its control, and a susceptibility to ion-exchange in hard waters which deteriorate the flameproofness. This type of treatment has been studied both by the inventors and under a Quartermaster Research Project at Columbia University, and intensive work to overcome these difficulties and improve the finish is in progress.

Another type of treatment which shows some promise as a durable finish uses the unique principle of increasing the dielectric constant of an organic solvent by the addition of water to precipitate a water-insoluble flame-retardant material within the fibers. While this process introduces the problems of double-bath treatment and suitable solvent recovery systems, which tend to make it costly, it does produce a durable finish of reasonably good characteristics.

Much practical evaluation work has been done on various flameproofed fabrics. Methods of testing have been developed to reveal what weaknesses a treatment might develop in combat use. Practical tests are conducted both in special laboratory equipment where all conditions can be carefully controlled and in the open where some special circumstances of nature can be utilized with or without some degree of control. For instance long-range tentage tests are conducted under temperate, tropic and desert exposure conditions. Relative flammability of tentage has been determined by setting up tents and attempting to ignite them by a variety of means. Clothing treatments have been tested for the effect of sweat by being worn in a jungle room, for the effect of rain in a rain-making room, for the effect of sea water by actual tests in the ocean, and for endurance by being worn and laundered until the fabric or finish failed under various normal or accelerated conditions of wear such as wearing on a specially designed combat course.

The enemy textile industries apparently were not as far advanced in

flameproofing methods as were the industries of this country. No samples of a superior, durably flameproofed fabric were ever discovered by intelligence services and the state of the art in Germany as determined by Combined Intelligence Objectives Subcommittee experts can be summarized as being confined to water-soluble salts and attempts to bind these salts permanently into a fabric by resin formation, principally by the use of urea-formaldehyde type resin.

The following chapters are a comprehensive presentation of the combined experiences of the Armed Services in developing, evaluating and utilizing flameproofed textile fabrics. They include descriptions of the programs undertaken by the Quartermaster Corps in the development of flameproofed tentage and clothing fabrics, similar application studies pertaining to camouflage fabrics as undertaken by the Corps of Engineers, and the program conducted by the Navy in the development of flame-resistant life jackets. In conclusion, a final chapter considers the many applications of flameproofing in the field of civilian fabrics.

While much progress has been made, the ideal solution or solutions of the problem, which meet all the requirements for flameproofed fabrics intended for either military or civilian purposes, is yet to be achieved. Research must continue.

# Chapter VI

## Applications to Army Clothing Fabrics

Of the many important applications which flameproofing treatments find in the field of textile fabrics, certainly one of the principal uses lies in the processing of garment fabrics. In the past, however, commercial flameproofing has been limited, for the most part, to decorative fabrics for both indoor and outdoor use. These items have included awnings, upholstery covers, curtains, drapes and the like. Outstanding exceptions to this group are tentage and tarpaulin fabrics which have long been treated so as to be resistant to flaming combustion.

At the present time it appears that serious consideration must be given to the flameproofing of fabrics intended for clothing purposes. In recent years, the Armed Services have carried out extensive studies of the application of flameproofing treatments to fabrics intended for use in military uniforms. It is highly probable that their findings will be of some assistance to those engaged in the fabrication and finishing of civilian garments. Accordingly, the following pages reveal the experiences of the Quartermaster Corps in the application of flameproofing treatments to army clothing fabrics. At the same time, the extensive tests performed on the numerous different retardants afford a fairly comprehensive comparison of the relative performances of flameproofing compounds and mixtures.

### A. GENERAL REQUIREMENTS

*E. Folger Taylor*

The main objective to be achieved by flameproofing Army clothing is to prevent ignition and free combustion of the garments when they come in contact with an outside heat source. Presumably this is the same objective that must be achieved in flameproofing civilian garments, the only difference being that the soldier is, perhaps, exposed to more unusual sources of fire such as shell burst and incendiary weapons.

For military clothing purposes the requirements of a flameproofing treatment can be divided into five categories. First, the treatment must provide maximum resistance to ignition, free flaming and afterglow. Maximum resistance can be defined in terms of time of afterflaming and time

of afterglow as determined by a standardized flame test such as the 45°-Microburner or Vertical-Bunsen burner tests. Obviously, for maximum resistance a zero value for both these times is required; however, a treatment which shows only a few seconds of afterflaming and afterglow can be considered very good. For the ideal treatment the flameproof qualities of the fabric will not deteriorate during storage or wearing of the garments.

The second requirement of a flameproofing treatment is that it must not decrease the comfort and the environmental protection which a garment made of untreated fabric affords the wearer. The soldier invariably discards at the first opportunity those pieces of equipment or uniform that give him discomfort or hinder his normal movements. Thus, if a flameproofing treatment results in a stiff, boardy feeling garment, or imposes an additional heat load or scratches and is otherwise uncomfortable, a soldier will wear it as little as possible, even though he knows that he is surrendering protection from a serious but transient danger. With regard to environmental protection, the treated garment should not decrease the protection to sun, wind, rain, snow, dirt and mud that the untreated garment affords.

The third requirement is that the physical properties of the garment fabric should not be impaired by the treatment. There should be no initial reduction of the tensile strength or the tear resistance of the fabric. Neither should these properties deteriorate in storage any faster than the untreated fabric. The length of time that a flameproof garment can be worn in the performance of certain tasks should be no less than that of untreated garments. In addition, the treatment should not detract from the appearance of the fabric. Garments made of treated fabric should have the same neat appearance as garments made of the untreated fabric.

The fourth requirement consists of a group of characteristics which the ideal treatment must have. The treatment should be resistant to laundering and dry cleaning for the life of the garment. While these characteristics could be classed as part of the first requirement that specifies the treatment shall not deteriorate during the life of the garment, it is of such importance that it must be emphasized as a special characteristic. Resistance to repeated launderings is undoubtedly the most difficult problem to solve with any flameproofing treatment which does not modify the properties of the cloth to such an extent that it is undesirable as a clothing fabric. The treatment should not break up and come off as a dust (dusting) nor rub off as a smear (crocking). The flameproofing treatment should also be non-toxic to the wearer under all conditions of use. This is an important consideration and extensive tests must be performed to show that no primary or secondary skin irritations, sensitization to skin irritation, or systemic poisoning result from contact of the treated fabric with the body. It is obvious that an irritant or poisonous treatment must

be rejected for use on clothing, and further, that the use of an irritant finish for other items is questionable because of the attendant danger to manufacturing personnel handling the cloth.

The fifth requirement concerns the compatibility of a flameproofing treatment with other impregnations of clothing which are of military importance. One such impregnation is with anti-gas chemicals to protect against vesicant gases; another is with water repellents to give rain protection; other impregnations give protection against disease-carrying insects. The ideal flameproofing process will be compatible with these treatments so that there will be no deterioration of the dominant protection afforded by each. Neither should the combination of treatments induce skin irritation or other toxic effects.

The requirements which have been set up for flameproofing treatments obviously are those which are considered ideal. Fulfilling of all the requirements would give the ideal military clothing fabric treatment. Partial fulfillment of the requirements, such as one or two seconds of afterflame and several seconds of afterglow in the 45°-Microburner flame test, a slight reduction in wearing qualities and a slightly increased heat load might give a fabric serviceable for some military uses but still open to development.

## B. RELATIVE SUITABILITY OF TREATMENTS

The general requirements for the performance of a flameproofed fabric have been previously outlined in Chapter I and the specific demands on a fabric intended for use in articles of military clothing discussed in the preceding section. Just what performance requirements are prescribed for a flameproofing agent or treated fabric were outlined in Chapter IV along with the test procedures employed in the comparative evaluation of different agents and treatments. In a practical study of the relative efficiencies of several different retardants, the comparison must include not only the resistance to the propagation of afterflaming and afterglow but also the effect of the retardant upon the strength and porosity characteristics of the fabric and, in the case of durable treatments, the extent to which the retardant is rendered ineffective by leaching or laundering. Surveying the entire field of available flameproofing treatments, including both the temporary and durable types, it is relatively simple by laboratory tests to separate the effective treatments from those which are plainly inferior and unsatisfactory. Which single agent or process is then selected from this group as the one desired for a particular application is dependent to a great extent upon the end-use of the treated fabric and the performance requirements set up for that fabric. Suffice it to say that there is, as yet, no perfect flameproofing treatment which imparts the desired characteristics of permanent flame and glow retardancy to the fabric without impairing in any way the other desirable fabric characteristics.

## 1. Laboratory Evaluations

*Robert W. Little*

Since, in comparing the performance of different flameproofing agents in the laboratory, they fall naturally into two groups consisting of the water-soluble or temporary treatments on the one hand and the insoluble, more permanent treatments on the other, the comparative laboratory evaluations described in the following sections have been separated into these same two groups.

### a. Temporary Treatments

In the search for a temporary flameproofing treatment for the processing of Army clothing, one of the first steps taken is logically a comparative study of the already available retardants as reported upon in the technical, trade and patent literature. Included in this group are many commercial preparations which demand consideration due to their effectiveness and availability to the textile industry. Since it is not the intended function of this volume to serve as a referee of the relative merits of the various industrial preparations, no direct references have been made to the trade names, exact compositions or manufacturers of these commercial products. It is sufficient to indicate the general composition of the products cited stating the major components of the mixtures.

It is not possible to present in any one publication a comprehensive comparison of the relative efficiencies of all of the water-soluble flameproofing agents developed to date. The compounds and mixtures evaluated in the following pages have therefore been restricted to the most efficient of the water-soluble group, attempting to compare the general types of agents available. Three commercial preparations have been included in the group of retardants discussed. Commercial Product A is a balanced mixture of the ammonium salts of sulfamic and phosphoric acids. The major components of Commercial Product E are hydrated aluminum sulfate and monoammonium phosphate. The third commercial retardant, Product F, has as its major components monosodium phosphate, ammonium chloride and a borate.

In the evaluation of any flameproofing treatment the characteristic of primary importance is the ability of the compound or mixture to prevent afterflaming and afterglow when the treated fabric is exposed to an igniting flame. In the course of the following discussions it will be assumed that afterflaming and afterglow are equally important and equally undesirable. In the case of some specific practical applications this may not be the case. In comparing the relative flameproofing efficiencies of several retardant mixtures it is insufficient to select a single solution concentration and

Table 1. Variation of Flameproofness with Add-On for the Better of the Water-Soluble Retardants

| Retardant | Add-On % | Flame Test | Afterflame sec. | Afterglow sec. | Char Area, in² or Char Length, in. |
|---|---|---|---|---|---|
| Borax : Boric Acid (7 : 3) | 5.1 | 45°-Micro | 0 | 362 | 4.0 in² |
| | 7.5 | " | 0 | 149 | 2.2 |
| | 9.5 | " | 0 | 140 | 2.2 |
| | 11.3 | " | 0 | 77 | 2.0 |
| | 12.8 | " | 0 | 34 | 1.6 |
| | 14.5 | " | 0 | 17 | 1.6 |
| | 5.4 | Vert-Bunsen | 0 | 775 | 6.0 in. |
| | 7.8 | " | 0 | 348 | 3.5 |
| | 9.2 | " | 0 | 206 | 2.7 |
| | 11.4 | " | 0 | 155 | 2.5 |
| | 13.4 | " | 0 | 161 | 2.5 |
| | 14.4 | " | 0 | 62 | 2.4 |
| Borax : Boric Acid (1 : 1) | 5.3 | 45°-Micro | 0 | 138 | 2.5 in² |
| | 6.7 | " | 0 | 107 | 1.9 |
| | 7.7 | " | 0 | 25 | 1.7 |
| | 9.1 | " | 0 | 13 | 1.6 |
| | 12.3 | " | 0 | 10 | 1.6 |
| | 15.3 | " | 0 | 18 | 1.7 |
| | 5.0 | Vert-Bunsen | 0 | 265 | 4.1 in. |
| | 6.9 | " | 0 | 257 | 3.2 |
| | 8.3 | " | 0 | 173 | 2.7 |
| | 9.5 | " | 0 | 38 | 2.9 |
| | 12.1 | " | 0 | 25 | 2.5 |
| | 14.8 | " | 0 | 19 | 2.9 |
| Diammonium Phosphate | 4.6 | 45°-Micro | 26 | — | B.E.* |
| | 7.0 | " | 0 | 0 | 4.3 in² |
| | 9.3 | " | 0 | 0 | 4.2 |
| | 11.2 | " | 0 | 0 | 3.7 |
| | 13.8 | " | 0 | 0 | 3.4 |
| | 17.3 | " | 0 | 0 | 2.8 |
| | 4.5 | Vert-Bunsen | 23 | — | B.E. |
| | 6.8 | " | 0 | 0 | 4.9 in. |
| | 8.9 | " | 0 | 0 | 4.0 |
| | 10.7 | " | 0 | 0 | 3.7 |
| | 13.3 | " | 0 | 0 | 3.2 |
| | 17.0 | " | 0 | 0 | 2.9 |

* B.E.—Burned to the end.

*(Continued next page)*

Table 1. Variation of Flameproofness with Add-On for the Better of the Water-Soluble Retardants (*Continued*)

| Retardant | Add-On % | Flame Test | Afterflame sec. | Afterglow sec. | Char Area, in $^2$ or Char Length, in. |
|---|---|---|---|---|---|
| Ammonium Dihydrogen Phosphate | 6.7 | 45°-Micro | 1 | 0 | 5.3 in $^2$ |
| | 7.8 | " | 0 | 0 | 4.6 |
| | 10.0 | " | 0 | 0 | 3.9 |
| | 10.5 | " | 0 | 0 | 4.0 |
| | 14.9 | " | 0 | 0 | 3.1 |
| | 19.8 | " | 0 | 0 | 2.6 |
| | 6.4 | Vert-Bunsen | 0 | 0 | 5.0 in. |
| | 7.7 | " | 0 | 0 | 4.2 |
| | 9.2 | " | 0 | 0 | 4.2 |
| | 10.0 | " | 0 | 0 | 3.4 |
| | 14.0 | " | 0 | 0 | 3.1 |
| | 18.6 | " | 0 | 0 | 2.7 |
| Borax : Boric Acid : Diammonium Phosphate (7 : 3 : 5) | 3.6 | 45°-Micro | 45 | — | B.E.* |
| | 7.4 | " | 0 | 8 | 1.9 in $^2$ |
| | 9.5 | " | 0 | 6 | 1.9 |
| | 13.6 | " | 0 | 4 | 1.8 |
| | 3.1 | Vert-Bunsen | 25 | — | B.E. |
| | 6.7 | " | 0 | 12 | 3.5 in. |
| | 8.7 | " | 0 | 9 | 3.3 |
| | 12.4 | " | 0 | 7 | 3.1 |
| Borax : Boric Acid : Diammonium Phosphate (5 : 5 : 1) | 7.4 | 45°-Micro | 33 | — | B.E. |
| | 10.0 | " | 0 | 15 | 1.8 in $^2$ |
| | 12.0 | " | 0 | 13 | 1.7 |
| | 14.4 | " | 0 | 8 | 1.7 |
| | 18.2 | " | 0 | 3 | 1.6 |
| | 7.0 | Vert-Bunsen | 1 | 112 | 3.7 in. |
| | 9.2 | " | 0 | 61 | 3.2 |
| | 11.3 | " | 0 | 13 | 2.9 |
| | 13.1 | " | 0 | 13 | 2.6 |
| | 16.9 | " | 0 | 6 | 2.5 |
| Borax : Diammonium Phosphate (1 : 1) | 8.7 | 45°-Micro | 7 | 2 | 2.2 in $^2$ |
| | 11.2 | " | 0 | 0 | 1.7 |
| | 17.3 | " | 0 | 0 | 1.1 |
| | 7.9 | Vert-Bunsen | 0 | 2 | 3.3 in. |
| | 10.9 | " | 0 | 2 | 3.3 |
| | 16.7 | " | 0 | 2 | 2.7 |

* B.E.—Burned to the end.

(*Continued next page*)

Table 1. Variation of Flameproofness with Add-On for the Better of the Water-Soluble Retardants (*Continued*)

| Retardant | Add-On % | Flame Test | Afterflame sec. | Afterglow sec. | Char Area, in $^2$ or Char Length, in. |
|---|---|---|---|---|---|
| Ammonium Sulfamate | 4.3 | 45°-Micro | 7 | — | B.E.* |
| | 6.8 | " | 0 | 562 | 7.7 in $^2$ |
| | 10.4 | " | 0 | 473 | 5.9 |
| | 15.2 | " | 0 | 398 | 4.7 |
| | 21.2 | " | 0 | 309 | 3.0 |
| | 27.8 | " | 0 | 243 | 2.6 |
| | 4.0 | Vert-Bunsen | 0 | — | B.E. |
| | 6.4 | " | 0 | 780 | 6.6 in. |
| | 9.8 | " | 0 | 642 | 5.1 |
| | 14.5 | " | 0 | 366 | 3.4 |
| | 19.1 | " | 0 | 298 | 3.0 |
| | 26.8 | " | 0 | 276 | 2.6 |
| Sodium Tungstate | 6.2 | 45°-Micro | 15 | — | B.E. |
| | 9.2 | " | 1 | 241 | 4.1 in $^2$ |
| | 12.7 | " | 0 | 145 | 2.7 |
| | 16.3 | " | 0 | 115 | 2.6 |
| | 20.3 | " | 0 | 129 | 2.1 |
| | 27.4 | " | 0 | 134 | 1.8 |
| | 8.5 | Vert-Bunsen | 0 | — | B.E. |
| | 11.7 | " | 0 | 200 | 3.6 in. |
| | 14.9 | " | 0 | 191 | 3.4 |
| | 17.7 | " | 0 | 210 | 3.1 |
| | 24.4 | " | 0 | 195 | 2.9 |
| Sodium Dihydrogen Phosphate | 13.5 | 45°-Micro | 55 | — | B.E. |
| | 16.9 | " | 1 | 0 | 2.4 in $^2$ |
| | 20.9 | " | 0 | 0 | 1.8 |
| | 28.5 | " | 0 | 0 | 1.5 |
| | 12.5 | Vert-Bunsen | 45 | — | B.E. |
| | 17.0 | " | 0 | 2 | 3.6 in. |
| | 19.8 | " | 0 | 2 | 3.1 |
| | 26.9 | " | 0 | 2 | 2.9 |
| Ammonium Sulfate | 10.1 | 45°-Micro | 0 | 645 | 9.5 in $^2$ |
| | 13.1 | " | 0 | 628 | 7.3 |
| | 15.6 | " | 0 | 475 | 5.2 |
| | 17.9 | " | 0 | 424 | 4.2 |
| | 22.0 | " | 0 | 298 | 2.9 |
| | 27.7 | " | 0 | 267 | 2.4 |
| | 9.5 | Vert-Bunsen | 0 | — | B.E. |
| | 14.9 | " | 0 | 790 | 5.6 in. |
| | 17.3 | " | 0 | 549 | 4.0 |
| | 21.5 | " | 0 | 375 | 3.0 |
| | 26.5 | " | 0 | 258 | 2.9 |

* B.E.—Burned to the end.

(*Continued next page*)

Table 1. Variation of Flameproofness with Add-On for the Better of the Water-Soluble Retardants (*Continued*)

| Retardant | Add-On % | Flame Test | Afterflame sec. | Afterglow sec. | Char Area, in² or Char Length, in. |
|---|---|---|---|---|---|
| Ammonium Bromide | 10 | 45°-Micro | 0 | 0 | 3.1 in² |
| | 20 | " | 0 | 0 | 2.5 |
| | 10 | Vert-Bunsen | 0 | 142 | 3.6 in. |
| | 20 | " | 0 | 11 | 2.7 |
| Ammonium Iodide | 12 | 45°-Micro | 0 | 2 | 3.1 in² |
| | 16 | " | 0 | 0 | 3.4 |
| | 24 | " | 0 | 0 | 3.0 |
| | 12 | Vert-Bunsen | 0 | 60 | 4.2 in. |
| | 16 | " | 0 | 9 | 3.3 |
| | 24 | " | 0 | 6 | 3.0 |
| Commercial Product A | 5.4 | 45°-Micro | 0 | 34 | B.E.* |
| | 10.9 | " | 0 | 0 | 3.5 in² |
| | 16.7 | " | 0 | 0 | 2.8 |
| | 22.3 | " | 0 | 0 | 2.5 |
| | 5.1 | Vert-Bunsen | 24 | 0 | B.E. |
| | 10.5 | " | 0 | 0 | 3.6 in. |
| | 16.3 | " | 0 | 0 | 2.9 |
| | 21.4 | " | 0 | 0 | 2.7 |
| Commercial Product E | 7.4 | 45°-Micro | 26 | 0 | B.E. |
| | 11.0 | " | 0 | 0 | 3.6 in² |
| | 16.6 | " | 0 | 0 | 2.7 |
| | 19.7 | " | 0 | 0 | 2.1 |
| | 7.4 | Vert-Bunsen | 0 | 0 | 4.4 in. |
| | 11.0 | " | 0 | 0 | 3.7 |
| | 16.6 | " | 0 | 0 | 2.6 |
| | 19.7 | " | 0 | 0 | 2.9 |
| Commercial Product F | 4.4 | 45°-Micro | 41 | 0 | B.E. |
| | 8.8 | " | 0 | 4 | 3.3 in² |
| | 14.7 | " | 0 | 2 | 2.5 |
| | 19.6 | " | 0 | 3 | 2.1 |
| | 4.7 | Vert-Bunsen | Completely consumed, no afterglow | | |
| | 8.8 | " | 0 | 2 | 3.7 in. |
| | 15.5 | " | 0 | 3 | 2.6 |
| | 20.8 | " | 0 | 2 | 2.5 |

* B.E.—Burned to the end.

compare the members of the group at that one add-on. As is often the case, it may be that one retardant is markedly superior at a low add-on while when present in slightly greater amount several agents may be equally effective. Where a slightly higher add-on is not objectionable these retardants may then be considered equally satisfactory.

**Relative Flameproofing Efficiencies.** The flameproofing characteristics of a representative group of the better water-soluble retardants are compared in Table 1 over an add-on range from 5 to 25%. The mixtures of borax and boric acid are obviously the most efficient flame retardants, effectively preventing any afterflaming at add-ons as low as 5%. The afterflaming times and extent of the chars both attest to the ability of these mixtures to prevent flaming both in the presence and absence of the igniting flame. The rest of the agents shown are comparable in their flame-retarding capacities, the borax-boric acid-phosphate mixtures being somewhat superior to ammonium sulfamate and sulfate and the ammonium halides. The least effective of this select group are sodium tungstate and phosphate. The commercial mixtures of ammonium sulfamate and phosphate, aluminum sulfate and ammonium dihydrogen phosphate, and ammonium chloride, sodium phosphate and borate are among the better flame retardants, being comparable to the borax-boric acid mixtures.

The times of afterglow in Table 1 indicate that practically the only effective glow retardants found are the phosphates, the outstanding examples being the ammonium salts. Monosodium phosphate is fairly effective but, as was shown in Chapter V, this is not the case with the disodium salt. The ammonium halides exhibit appreciable glow-retarding properties but, like boric acid, are markedly inferior to the phosphate salts of weak bases. The glow-preventing tendencies of boric acid are indicated by a comparison of the 7:3 and 1:1 mixtures with borax where the glow retardancy is proportional to the boric acid present in the mixture. A similar comparison of the other mixtures, including the commercial preparations, indicates that in every case the glow retardancy of the flameproofing agent is attributable to the phosphate, the efficiency being proportional to the amount of phosphate present.

The char area or char length measurement in the standard flame tests represents the extent of thermal degradation in the presence of the flame. Choosing this as the criterion of flameproofness, the retardants may be comparatively evaluated as shown in Figure 1. The order of efficiency thus obtained is very similar to that previously stated, the borate mixtures being the most effective, those with added phosphate slightly less so, and the sulfamate-phosphate type the least effective. It should be borne in mind here that we are attempting to differentiate, not between retardants of greatly different orders of efficiency but between a group of effective agents which possess very similar flame-retardant properties. It is worth noting in Figure 1 that, as was stated in the description of flame test

methods in Chapter IV, the 45°-Microburner flame test allows for a much better comparison of relative flame retardancies than does the Vertical-Bunsen test.

**Comparisons at Equal Add-ons.** In order to compare the efficiencies of these water-soluble treatments when present on the fabric in equal quantities, the flame test data for an add-on of approximately 10% is presented in Table 2. It is plainly apparent that under these conditions

Table 2. Relative Efficiencies of Flameproofing Agents at 10% Add-On

| Retardant | Flame Test | Afterflame sec. | Afterglow sec. | Char Area, in² or Char Length, in. |
|---|---|---|---|---|
| Borax : Boric Acid (7 : 3) | 45°-Micro | 0 | 105 | 2.1 in² |
| Borax : Boric Acid (1 : 1) | " | 0 | 13 | 1.6 |
| Diammonium Phosphate | " | 0 | 0 | 4.0 |
| Ammonium Dihydrogen Phosphate | " | 0 | 0 | 4.1 |
| Borax : Boric Acid : Diammonium Phosphate (7 : 3 : 5) | " | 0 | 6 | 1.9 |
| Borax : Boric Acid : Diammonium Phosphate (5 : 5 : 1) | " | 0 | 15 | 1.8 |
| Ammonium Sulfamate | " | 0 | 480 | 6.3 |
| Commercial Product A | " | 0 | 0 | 3.7 |
| Borax : Boric Acid (7 : 3) | Vert-Bunsen | 0 | 190 | 2.6 in. |
| Borax : Boric Acid (1 : 1) | " | 0 | 32 | 2.7 |
| Diammonium Phosphate | " | 0 | 0 | 3.9 |
| Ammonium Dihydrogen Phosphate | " | 0 | 0 | 3.4 |
| Borax : Boric Acid : Diammonium Phosphate (7 : 3 : 5) | " | 0 | 8 | 3.2 |
| Borax : Boric Acid : Diammonium Phosphate (5 : 5 : 1) | " | 0 | 43 | 3.1 |
| Ammonium Sulfamate | " | 0 | 550 | 5.0 |
| Commercial Product A | " | 0 | 0 | 3.7 |

the flameproofing agents shown are equally effective in the prevention of afterflaming but differ greatly in their abilities to prevent afterglow and the thermal degradation which occurs in the presence of the flame. Considering the data presented thus far it is possible to compare the relative efficiencies of the flameproofing agents cited on the basis of the initial flameproofness of the treated fabric. It has been assumed that, in the case of fabrics for clothing purposes, the glowing of the charred fabric is equally as objectionable as afterflaming. On this basis, the water-soluble retardants of Table 1 can be separated into two groups. The most efficient flameproofing agents considered would include borax-diammonium phosphate (1:1), ammonium sulfamate-diammonium phosphate, aluminum

sulfate-monoammonium phosphate, ammonium chloride-sodium phosphate-borax, ammonium phosphate alone either as the mono- or diammonium salt and the 5:5:1 and 7:3:5 mixtures of borax-boric acid-diammonium phosphate. The second group of less effective retardants includes the

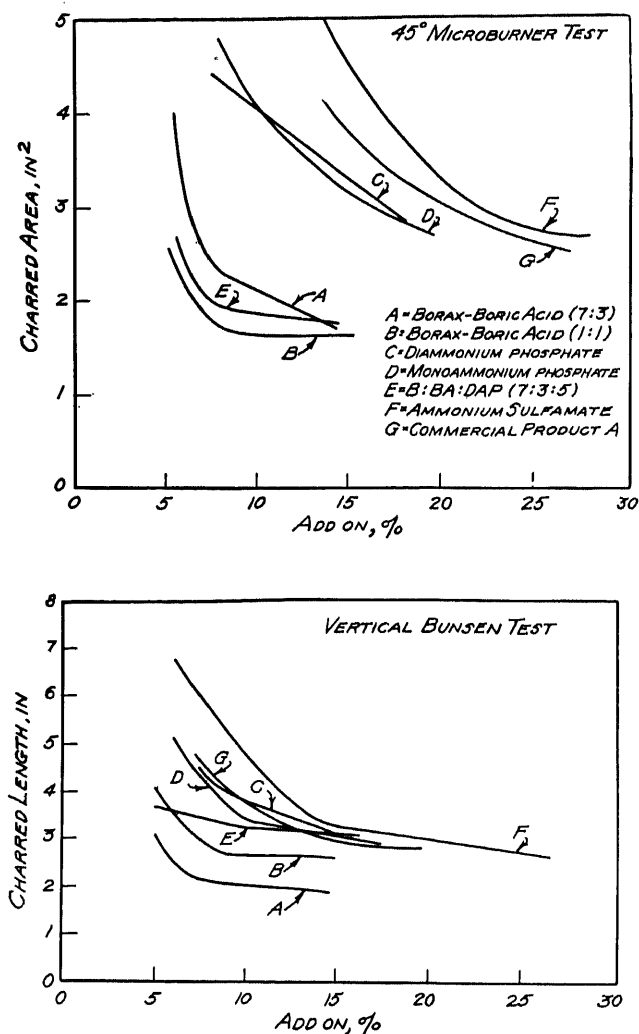



Figure 1. Relative efficiencies of water-soluble retardants based on char area and char length.

borax-boric acid mixtures, the ammonium halides, ammonium sulfamate, ammonium sulfate, monosodium phosphate and sodium tungstate.

**Effect on Desirable Textile Properties: Hand.** In the flameproofing of clothing fabrics it is required that the treatment not only impart a high

degree of resistance to both flaming and glowing but also that the other desirable characteristics of the fabric shall not be excessively impaired. One fabric property which cannot be quantitatively defined, but which is important particularly in articles of clothing, is the texture, feel or "hand" of the cloth. The borate mixtures do impart a slight harshness to the cloth, and, in contrast, the sulfamates and their mixtures function somewhat as softening agents producing a slightly softer finish. In general, however, the application of any of the water-soluble flameproofing treatments does not so greatly influence the hand of the fabric as to condemn the use of the treatment.

**Resistance to Moisture Vapor Transfer.** The moisture vapor permeability of a fabric has been shown to be related to the heat load which a garment constructed of that fabric would impose upon the wearer. It is desirable, therefore, that the addition of the flameproofing treatment does not appreciably increase the resistance of the fabric to the transmission of moisture vapor. The intrinsic resistance of 8.5 oz. herringbone twill treated with representative water-soluble retardants are shown in Table 3 as

Table 3. Intrinsic Resistance of Flameproofed Fabrics to the Passage of Moisture Vapor

| Treatment | Add-On % | Intrinsic Resistance equiv. cm. of still air |
|---|---|---|
| None (8.5 oz. Herringbone Twill) | — | 0.14 |
| Borax : Boric Acid (7 : 3) | 12.4 | 0.18 |
| Borax : Boric Acid (1 : 1) | 15.9 | 0.11 |
| Diammonium Phosphate | 16.0 | 0.18 |
| Ammonium Dihydrogen Phosphate | 15.4 | 0.11 |
| Borax : Boric Acid : Diammonium Phosphate (7 : 3 : 5) | 14.4 | 0.17 |
| Borax : Boric Acid : Diammonium Phosphate (5 : 5 : 1) | 15.1 | 0.16 |
| Ammonium Sulfamate | 28.0 | 0.11 |
| Commercial Product A | 13.6 | 0.20 |

compared with that of the untreated cloth. As was pointed out in the discussion of the laboratory test method in Chapter IV, the precision of these measurements is approximately ± 0.05 cm. Taking this into consideration and also comparing these values with those of the durable treatments discussed in the following section (Table 10), it is apparent that the water-soluble treatments do not appreciably increase the resistance to moisture vapor. Comparing the laboratory test data with the findings of heat load experiments discussed in a later section, it is unlikely that any of these temporary treatments would significantly influence the heat load imposed by the garment upon the wearer.

**Fabric Strength.** Regardless of the effectiveness of a flameproofing agent in preventing the flaming and glowing of the fabric, the treatment would be of little value if, in the course of attaining the desired flameproof characteristics, it at the same time appreciably reduced the serviceability of the garment. In this respect, it is of primary importance that the appli-

cation of the retardant does not radically reduce the strength characteristics of the fabric. In nearly every case the treatment with a water-soluble agent does cause a slight decrease in tensile strength (see Table 5). The tensile loss is in the order of 10% ranging from 5 to 15% and again, considering the precision of the tensile strength measurement, is not considered to be excessive.

**Stability Under Accelerated Conditions.** In the case of the water-soluble flameproofing agents under consideration, it is presumed that the treatment is only temporary in nature and will be impaired or completely destroyed by exposure to any leaching conditions due to rain, immersion, laundering or even excessive perspiration. The treatments are such that they will require periodic reprocessing in order to maintain the desired flameproof characteristics. It is highly desirable, however, that the treated fabric retain its retardancy and tensile strength throughout the period of normal use and, in the case of military clothing, through any period of storage prior to issue. With this in mind, representative water-soluble treatments were exposed to accelerated aging tests designed to simulate the conditions of hot-humid storage and hot-dry storage which might be encountered in the course of military operations. The data presented in Tables 4 and 5 indicate that under these extreme conditions many of the temporary treatments do suffer an appreciable loss of either flameproofness or fabric strength.

The exposure to high temperature and high humidity causes a decrease in the flameproofness of fabrics treated with the borate mixtures, particularly when ammonium phosphate has been incorporated as a glow-retarding ingredient. The mixtures of borax and boric acid are only slightly affected in the form of an increase in afterglowing tendency. This would appear to be attributable to a loss of boric acid through volatilization. When ammonium phosphate is also present the flameproofness is completely destroyed. The data on the loss in weight of these fabrics in the course of the storage (Table 5) indicate that an appreciable amount of the retardant has been lost by volatilization. The effects shown could be attributed to a rapid sublimation of boric acid under these conditions. In the case of the 7:3:5 and 5:5:1 mixtures with ammonium phosphate, the loss of ammonia and subsequent formation of the acid phosphate would not only accelerate the sublimation of boric acid but would also result in the interaction between borax and the phosphate with the formation of additional amounts of volatile boric acid leaving a residue of sodium phosphate. The flame test data on the aged specimens of the 7:3:5 and 5:5:1 mixtures are characteristic of the effectiveness of sodium phosphate and borax respectively at add-ons of 7 to 8%. The ammonium phosphates alone do not suffer any loss of effectiveness under these conditions nor does the sulfamate-phosphate mixture as exemplified by commercial product A. Ammonium sulfamate exhibits a slight but negligible increase in its

Table 4. Effect of High Temperature and High Humidity Upon the Flameproofness of Fabrics Treated With Water-Soluble Retardants

(45°-*Microburner Flame Test*)

| Tendering Treatment | | Borax: Boric Acid (7:3) | Borax: Boric Acid (1:1) | Diam-monium Phosphate | Ammonium Dihydrogen Phosphate | Borax: Boric Acid: Diammonium Phosphate (7:3:5) | Borax: Boric Acid: Diammonium Phosphate (5:5:1) | Ammonium Sulfamate | Commercial Product A |
|---|---|---|---|---|---|---|---|---|---|
| | % Add-On | 12.8 | 15.1 | 14.9 | 15.4 | 14.4 | 15.1 | 28.0 | 13.6 |
| None | Afterflame, sec. | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Afterglow, sec. | 17 | 10 | 1 | 0 | 4 | 8 | 14 | 1 |
| | Char Area, in² | 1.6 | 1.6 | 3.5 | 3.1 | 1.8 | 1.7 | 2.6 | 3.2 |
| 2 weeks; | Afterflame, sec. | 0 | 0 | 0 | 0 | 60 | 0 | 0 | 0 |
| 120° F., | Afterglow, sec. | 123 | 110 | 0 | 0 | 0 | 666 | 47 | 0 |
| 85% R.H. | Char Area, in² | 2.4 | 2.4 | 2.9 | 2.5 | Completely burned | Completely burned | 2.0 | 2.0 |
| 2 weeks; | Afterflame, sec. | 0 | 0 | 0 | 0 | 30 | 0 | 0 | 0 |
| 150° F., | Afterglow, sec. | 31 | 9 | 0 | 0 | 0 | 5 | 14 | 3 |
| dry | Char Area, in² | 2.3 | 2.1 | 4.2 | 3.0 | 7.6 | 2.1 | 2.5 | 1.9 |
| 3 weeks; | Afterflame, sec. | 0 | 0 | 0 | 0 | 23 | 0 | 0 | 0 |
| 150° F., | Afterglow, sec. | 11 | 9 | 0 | 0 | 0 | 6 | 11 | 0 |
| dry | Char Area, in² | 2.3 | 2.4 | 2.9 | 3.4 | 6.8 | 1.5 | 2.3 | 2.2 |
| 4 weeks; | Afterflame, sec. | 0 | 0 | 0 | 0 | 33 | 0 | 0 | 0 |
| 150° F., | Afterglow, sec. | 16 | 12 | 0 | 0 | 0 | 8 | 9 | 0 |
| dry | Char Area, in² | 1.5 | 2.3 | 3.2 | 3.7 | 7.1 | 1.4 | 2.4 | 1.9 |

Table 5. Effect of High Temperature and High Humidity Upon the Tensile Strength of Fabrics Treated With Water-Soluble Retardants

*(1-inch Raveled Strip Method)*

| Tendering Treatment | | Borax: Boric Acid (7:3) | Borax: Boric Acid (1:1) | Diammonium Phosphate | Ammonium Dihydrogen Phosphate | Borax: Boric Acid: Diammonium Phosphate (7:3:5) | Borax: Boric Acid: Diammonium Phosphate (5:5:1) | Ammonium Sulfamate | Commercial Product A |
|---|---|---|---|---|---|---|---|---|---|
| | % Add-On | 12.4 | 12.7 | 16.0 | 14.8 | 14.4 | 15.1 | 20.1 | 10.1 |
| None | Tensile Strength After Treatment | 118 | 113 | 118 | 113 | 120 | 116 | 126 | 126 |
| | % Loss in Strength on Treating | 11 | 14 | 11 | 14 | 9 | 12 | 5 | 5 |
| 2 weeks; 120° F., 85% R.H. | Tensile Strength After Tendering | 117 | 126 | 105 | 112 | 124 | 120 | 105 | 92 |
| | % Change in Strength on Tendering | − 1 | + 11 | − 10 | − 1 | + 3 | + 3 | − 17 | − 27 |
| | % Loss in Weight | 1 | 5 | 0 | 0 | 8 | 7 | 1 | 0 |
| 2 weeks; 150° F., dry | Tensile Strength After Tendering | 120 | 118 | 97 | 99 | 113 | 112 | 87 | 77 |
| | % Change in Strength on Tendering | + 2 | + 4 | − 18 | − 12 | − 6 | − 3 | − 31 | − 39 |
| | % Loss in Weight | 2 | 3 | 2 | 2 | 3 | 3 | 3 | 2 |

Table 5. Effect of High Temperature and High Humidity Upon the Tensile Strength of Fabrics Treated With Water-Soluble Retardants
*(1-inch Raveled Strip Method) (Continued)*

| Tendering Treatment | | Borax: Boric Acid (7:3) | Borax: Boric Acid (1:1) | Diammonium Phosphate | Ammonium Dihydrogen Phosphate | Borax: Boric Acid: Diammonium Phosphate (5:3:5) | Borax: Boric Acid: Diammonium Phosphate (5:5:1) | Ammonium Sulfamate | Commercial Product A |
|---|---|---|---|---|---|---|---|---|---|
| 3 weeks; 150° F., dry | Tensile Strength After Tendering | 118 | 117 | 80 | 92 | 110 | 119 | 55 | 73 |
| | % Change in Strength on Tendering | 0 | + 4 | − 32 | − 19 | − 8 | + 3 | − 56 | − 42 |
| | % Loss in Weight | 1 | 2 | 1 | 1 | 2 | 2 | 1 | 0 |
| 4 weeks; 150° F., dry | Tensile Strength After Tendering | 115 | 118 | 82 | 85 | 118 | 122 | 53 | 54 |
| | % Change in Strength on Tendering | − 3 | − 4 | − 31 | − 25 | − 2 | + 5 | − 58 | − 57 |
| | % Loss in Weight | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 1 |
| 2 weeks; 175° F., dry | Tensile Strength After Tendering | 116 | 103 | 36 | 33 | — | — | — | — |
| | % Change in Strength on Tendering | − 2 | − 9 | − 69 | − 71 | — | — | — | — |
| | % Loss in Weight | 0 | 0 | 0 | 0 | — | — | — | — |

afterglowing tendency. The hot-dry conditions of 150° F., dry are apparently less severe as far as the loss of flameproofness is concerned, none of the retardant treatments being significantly impaired with the exception of the 7:3:5 borate-phosphate mixture.

Upon consideration of the tensile strength data of Table 5, however, it is apparent that the fabrics which did not show any appreciable reduction of flameproofness are those most severely impaired with respect to fabric strength. Similarly, the borate mixtures, alone and with added phosphate, which suffered a loss of retardancy do not undergo any significant changes in tensile strength. The ammonium phosphates are incapable of withstanding more than two weeks of storage under these extreme conditions without suffering an excessive reduction in fabric strength. In this respect, it appears that the temperature is the governing factor since the conditions of 150° F., dry are more severe than those of 120° F. and 85% R.H. In the case of ammonium sulfamate and the commercial sulfamate-phosphate mixture, the strength losses are excessive even in the first two weeks of exposure.

**Stability Under Normal Conditions.** It would appear, therefore, that at least in the case of this particular group of water-soluble retardants, the temporary flameproofing treatments are relatively unstable and may be expected to suffer reductions in either flameproofness or fabric strength under the severe conditions which might be encountered in the course of military service. It might be suspected, also, that these phenomena are a time-temperature function and that the same changes might occur over an extended period of time at much lower temperatures. This was encountered in the case of one fabric specimen treated with the 7:3:5 mixture of borax, boric acid and diammonium phosphate. The sample of fabric, which was initially adequately flameproofed, was found after approximately one year's exposure to normal room conditions to have lost practically all of its flameproof characteristics. In an effort to determine the seriousness of this loss of retardancy at normal temperatures, several of the better water-soluble flameproofing agents were applied to 8.5 oz. herringbone twill and suspended for from two to three months under normal room conditions and also under the standard conditions of 70° F. and 65% R.H. The results of these experiments, which are summarized in Table 6, indicate that, under conditions of normal usage, fabrics treated with water-soluble flameproofing agents could be expected to serve satisfactorily for at least a two- or three-month period without any apparent loss of either retardancy or fabric strength.

Since the temporary flameproofing agents are applied with the intention of frequent reprocessing in order to retain flameproofness and also, since in most cases any fabric would be laundered at not more than two- or three-month intervals, it is believed that the water-soluble treatments will impart the desired flameproof characteristics to the fabric and retain

Table 6. The Influence of Prolonged Storage Upon the Flameproofness and Strength of Fabrics Treated With Some of the Better Water-Soluble Retardants

*(45°-Microburner Flame Test — 1-inch Raveled Strip Tensile Test)*

| Retardant | Add-On % | Storage Conditions | Months | 45° Flame Tests After-flame sec. | After-glow sec. | Char Area in² | Tensile lbs./in. strip |
|---|---|---|---|---|---|---|---|
| Borax : Boric Acid : Diammonium Phosphate (7 : 3 : 5) | 16 | 70° F./65% R.H. | 0 | 2 | 10 | 1.8 | 112 |
| | | | 1 | 0 | 12 | 1.3 | — |
| | | | 2 | 0 | 11 | 2.0 | 121 |
| | | | 3 | 0 | 11 | 2.2 | 114 |
| | 13 | Variable | 0 | 2 | 10 | 1.9 | 112 |
| | | | 1 | 1 | 14 | 1.4 | — |
| | | | 2 | 0 | 10 | 2.3 | 108 |
| | | | 3 | 0 | 11 | 2.7 | 104 |
| Commercial Product A | 16 | 75° F./65% R.H. | 0 | 0 | 5 | 2.1 | 125 |
| | | | 1 | 0 | 3 | 2.3 | 131 |
| | | | 2 | 0 | 4 | 2.2 | — |
| | | Variable | 0 | 0 | 0 | 2.1 | 123 |
| | | | 1 | 0 | 3 | 2.7 | 124 |
| Commercial Product E | 19 | 75° F./65% R.H. | 0 | 0 | 4 | 2.0 | 121 |
| | | | 1 | 0 | 5 | 2.1 | 130 |
| | | | 2 | 0 | 5 | 2.1 | 127 |
| | 20 | Variable | 0 | 0 | 5 | 1.6 | 120 |
| | | | 1 | 0 | 5 | 2.6 | 112 |
| | | | 2 | 0 | 6 | 2.3 | 112 |
| Commercial Product F | 15 | 75° F./65% R.H. | 0 | 0 | 13 | 2.5 | — |
| | | | 0.5 | 0 | 3 | 2.6 | 122 |
| | | | 2 | 0 | 15 | 2.8 | 127 |
| | | | 2.5 | 4 | 12 | 2.1 | — |
| | 14 | Variable | 0 | 1 | 12 | 2.4 | — |
| | | | 0.5 | 0 | 3 | 2.9 | 120 |
| | | | 2 | 0 | 16 | 3.1 | 105 |
| Borax : Diammonium Phosphate (1 : 1) | 14 | 70° F./65% R.H. | 0 | 0 | 10 | 2.3 | — |
| | | | 1 | 0 | 11 | 2.2 | 126 |
| | | | 2 | 0 | 9 | 2.3 | 128 |
| | | | 2.5 | 1 | 10 | 2.2 | — |
| | 14 | Variable | 0 | 0 | 7 | 1.8 | — |
| | | | 1 | 0 | 9 | 2.5 | 103 |
| | | | 2 | 0 | 13 | 2.6 | 114 |
| Untreated Regular Twill | 0 | — | — | Burns completely | — | — | 120 |

those properties as long as was intended, *i.e.* until the fabric or garment is laundered. If, however, the treated fabric is stored for several months prior to use or is exposed to the extremes of temperature and humidity for a prolonged period of time, it may suffer an appreciable loss of flameproofness or strength. In instances where it is known that these conditions

will be encountered, the selection of a temporary flameproofing treatment should be made with caution.

### b. Durable Treatments

The requirements for a flameproofing treatment for cotton fabrics have been pointed out in the early portions of this book and the specific requirements for Army clothing fabrics discussed earlier in this chapter. The flameproof characteristics can readily be attained by means of water-soluble retardants such as those just considered. These temporary treatments possess certain advantages over the more permanent type, the outstanding examples being the very low add-ons required and the ease with which the flameproofing procedure may be carried out. The latter makes it possible to impregnate garments in the field and thus permit the continued use of the many uniforms already fabricated and issued. It would obviously be preferable, however, if the flameproofing properties obtained by the treatments were permanent and could be retained by the garment throughout its period of service without the necessity of continued reprocessing. Thus far, the available flameproofing treatments which are capable of imparting more or less permanent protection to the garment have not been adaptable to a simple field treatment. The durable finishes are therefore generally applied to yard goods on an industrial scale and the clothing fabricated from the treated cloth.

As has been pointed out in the earlier fundamental sections, the available, durable flameproofing treatments can be divided into three general categories: those applied by means of a double impregnation or "double-bath" technique, the chlorinated wax-metallic oxide type which can be applied in the form of a suspension or emulsion, and the cellulose-ester type which is applied from aqueous solution and cured to form an inorganic ester of cellulose. The latter group has generally been referred to as being of the urea-phosphate type. Since the durable treatments are applied to the fabric with the intention that the retardancy will be retained throughout the life of the garment and will not require reprocessing, the evaluation studies of these treated fabrics, as outlined in Chapter IV, must include a measurement of the resistance of the treatment to the leaching action of rain, water immersion, perspiration, sea water and laundering. The urea-phosphate type treatments, although they are in many ways the most permanent of the durable group, are particularly susceptible to the action of high concentrations of alkali and alkaline earth ions and strongly alkaline solutions. The reasons for this instability have been clearly shown in the preceding chapter and will not be repeated here. That the removal of the effectiveness of the treatment is a function of the pH or alkali concentration and the time of contact with the solution is indicated in Table 7. Simple laboratory leaching tests have also shown that

Table 7. Effect of Leaching Upon the Flame Retardancy of Urea-Phosphate Type Fabrics

*(45°-Microburner Flame Test)*

| Solution | Leaching Treatment pH | Leaching Treatment Hours | Afterflame sec. | Afterglow sec. | Char Area in ² |
|---|---|---|---|---|---|
| None | — | — | 0 | 0 | 4.0 |
| Tap Water | 7.4 | 21 | 0 | 0 | 4.0 |
| | | 72 | 0 | 0 | 4.0 |
| 0.2% Ammonium Oleate | 8.6 | 16 | 0 | 1 | 3.9 |
| | | 73 | 0 | 1 | 3.9 |
| 0.2% Ammonium Oleate | 10.0 | 21 | 0 | 0 | 4.0 |
| + NaOH | | 75 | 35 | 0 | B.E.* |
| 1% Castile Soap + 5% | 11.8 | 21 | 52 | 0 | B.E. |
| $Na_2CO_3$ | | 75 | 61 | 0 | B.E. |

* Burned to the end.

a urea-phosphate type fabric may be leached indefinitely in distilled water without any apparent effect whereas long-term leaching in hard water will appreciably reduce the retardant properties. For this reason, the laboratory tests used in the evaluation of the permanence of durable flameproofing treatments include a rotation in synthetic sea water in addition to the standard leaching and laundering procedures.

**Nature of Finishes Considered.** The flameproofed fabrics compared in the following pages are representative of what is available in the way of durable treatments and have been developed by the research laboratories of different branches of the Armed Forces and by several textile finishing companies. In order to avoid repetition of the nature of the processes in each table, they will be discussed briefly at this time.

Fabric #1, developed in the course of the experimental work of N.R.C. Project Q.M.C. #27, is a double-bath impregnation with stannic tungstate. Essentially the process consists of consecutive immersions in 20% sodium tungstate and 20% stannic chloride, drying the fabric prior to immersion in the second bath. A more thorough discussion of the variables of this process has already been given in Chapter V and as was pointed out at that time, it may well be that the material actually deposited on the fabric should be pictured as a mixture of stannic oxide and tungstic acid rather than a molecular salt.

Commercial product Q must be considered as a double-bath treatment although the actual impregnation process is somewhat more complex. The treatment consists of a deposition of zinc borate on the fibres by immersions in solutions of borax and zinc chloride. In this case, however, the two salts are dissolved together in a glycol-type solvent and precipitation accomplished by exposure of the dried fabric to moisture. This may be

accomplished by immersing in water or by hanging in a humid atmosphere.

The solvent-suspension treated fabric developed by the Chemical Warfare Service Development Laboratories at the Massachusetts Institute of Technology was commercially treated with a mixture, the essential ingredients of which were a suspension of antimony oxide and Vinylite in an organic solvent such as methyl ethyl ketone.

Commercial products O and P were similarly treated with organic solvent suspensions of antimony oxide and Vinylite. In these instances, however, an attempt was made to prevent afterglow by the addition of zinc borate.

In the case of commercial product N both a vinyl chloride resin and chlorinated paraffin were suspended in an organic solvent along with antimony oxide and zinc borate.

Fabric #2 of N.R.C. Project Q.M.C. #27 was processed with a suspension of antimony oxide and zinc borate in a methyl ethyl ketone solution of Vinylite VYNS. Triphenyl phosphate was added as a plasticizer in order to improve the hand of the treated fabric (see Chapter V).

The flameproofed fabrics developed by the Technical Division of the Chemical Warfare Service at Edgewood Arsenal, Maryland, were processed with similar organic solvent suspensions, the flameproofing ingredients in which were zinc oxide and a chlorinated wax. In these cases, however, the picture is complicated by the presence of other ingredients which were included in order to render the fabric impervious to chemical warfare agents but which also undoubtedly contribute to the flameproofing properties of the mixture.

The emulsion treatment, listed as Fabric #3 of the Q.M.C. Project #27, consisted of a water-in-oil emulsion of 42% and 70% chlorinated paraffins, antimony oxide and zinc borate. The oil phase also included trichloroethylene as a diluent and Rezyl which serves a dual role as emulsifying agent and stabilizer.

The four urea-phosphate type fabrics included are of the general type discussed in the preceding chapter. The Q.M.C. #27 fabric #4 was treated with a 46% aqueous solution of urea and diammonium phosphate present in the molar ratio of 4.4:1. The commercial products differed with respect to the nature of the amido compound employed and also in the particular phosphate selected. In some cases formaldehyde was also included. Some variations existed in the times and temperatures employed in the curing process.

The durably treated fabrics were processed on commercial finishing equipment either in the form of a full-scale plant run or as an experimental process with the following exceptions. Q.M.C. #27 fabric #1 was purely a laboratory-scale experiment and the fabrics shown were treated according to the procedure outlined in Chapter IV. The two C.W.S. fabrics

from Edgewood Arsenal were of an experimental nature, #1 being applied in a Quartermaster portable laundry unit and #2 being processed in a standard commercial laundry washer. In these two cases, the flameproofing process was applied to finished articles of clothing, whereas all the other treatments described were applied to yard goods.

**Preliminary Comparative Evaluations.** The evaluation tests used as criteria of the relative efficiencies of durable flameproofing processes were described in Chapter IV. The preliminary evaluation data on the better permanent-type fabrics are summarized in Table 8 showing the initial flameproofness of the treated fabric and the resistance of each to leaching and laundering. Considering only the resistance of the fabrics to afterflaming, the majority of the better treatments are capable of retaining their flame-resisting properties through the preliminary leaching and laundering tests. The double-bath treatment with stannic tungstate is one exception, being appreciably impaired by a 5-minute leach in salt solution and completely destroyed by 3 launderings. The addition of a 3 to 4% overcoating with Resloom M–75 improves the glow resistance of the treated fabric and at the same time appreciably increases the permanence. When correctly applied, as illustrated by the commercial impregnation with zinc borate in product Q, it is possible to obtain a permanently flame-resistant fabric by means of a double-bath type of treatment. It is difficult, however, to find a suitable glow-resistant material which can be permanently bound into this type of finish without the use of greatly excessive add-ons.

The treatments employing a mixture of a metallic oxide and a chlorinated wax or resin possess excellent flame-retardant characteristics and are highly resistant to leaching or laundering. This is true whether applied in the form of a solvent suspension or as an emulsion. The only member of the group incapable of resisting 6 laundering treatments was commercial product P. The antimony oxide-chlorinated body type processes differ markedly, however, in their relative resistances to afterglow. When no glow-retarding component is added, as in the case of the C.W.S.–M.I.T. fabric, the afterglow is highly excessive ranging from 500 to 600 seconds in duration. The degradation of the fabric by this flameless combustion is actually enhanced by the presence of the metallic oxide and in general the afterglow not only consumes the charred area but also progresses into the uncharred portions of the specimen. The proper compounding of a semi-insoluble glow-retarding constitutent such as zinc borate reduces the afterglow to practically zero and the mixture is capable of retaining this property through six launderings in 0.5% G.I. soap. The emulsion and solvent suspension treatments developed under N.R.C. Project Q.M.C. #27 are examples of the efficacy of zinc borate in these pigment processes.

The excellent flame- and glow-resisting properties of fabrics processed by a urea-phosphate type treatment and the durability of the flameproof-

Table 8. The Relative Flameproofness and Permanence of the Durable Flame-Retardant Fabrics

*(45°-Microburner Flame Test)*

| Flameproofed Fabric | Add-On % | | Leaching or Laundering Treatment: None | 30 min. Leach in Tap Water | 5 min. Leach in 5% NaCl | 1 Laundering, 0.5% G.I. Soap | 3 Launderings, 0.5% G.I. Soap | 6 Launderings, 0.5% G.I. Soap |
|---|---|---|---|---|---|---|---|---|
| *Double Bath Treatments* | | | | | | | | |
| Q.M.C. #27, Fabric #1 | 29 | Afterflame, sec. | 2 | — | 6 | — | 44 | — |
| | | Afterglow, sec. | 2 | — | 23 | — | 116 | — |
| | | Char Area, in $^2$ | 3.7 | — | 7.1 | — | C.B.* | — |
| Q.M.C. #27, Fabric #1 over-coated with Resloom M–75 | 33.5 | Afterflame, sec. | 0 | — | — | — | — | 0 |
| | | Afterglow, sec. | 0 | — | — | — | — | 0 |
| | | Char Area, in $^2$ | 3.3 | — | — | — | — | 2.0 |
| Commercial Product Q | 29 | Afterflame, sec. | 0 | 0 | 0 | 0 | 0 | 0 |
| | | Afterglow, sec. | 0 | 0 | 0 | 0 | 84 | 163 |
| | | Char Area, in $^2$ | 3.6 | 3.5 | 3.6 | 2.9 | 2.0 | 2.2 |
| *Solvent Suspension Treatments* | | | | | | | | |
| C.W.S.–M.I.T. Fabric | 35 | Afterflame, sec. | 0 | 0 | 0 | 0 | 0 | 0 |
| | | Afterglow, sec. | 600 | 565 | 624 | 524 | 409 | 670 |
| | | Char Area, in $^2$ | 5.7 | 4.6 | 5.9 | 4.7 | 3.5 | 6.6 |
| Commercial Product O | 65 | Afterflame, sec. | 0 | 0 | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 31 | 0 | — | 21 | 0 | 18 |
| | | Char Area, in $^2$ | 2.8 | 1.3 | — | 1.9 | 1.2 | 2.5 |
| Commercial Product P | 47 | Afterflame, sec. | 0 | 0 | 0 | 0 | 0 | 14 |
| | | Afterglow, sec. | 25 | 24 | 29 | 46 | 51 | 69 |
| | | Char Area, in $^2$ | 3.7 | 2.7 | 2.8 | 3.0 | 2.6 | B.E.* |
| Commercial Product X | 35 | Afterflame, sec. | 0 | 0 | 0 | 0 | 0 | 0 |
| | | Afterglow, sec. | 28 | 37 | 30 | 28 | 35 | 32 |
| | | Char Area, in $^2$ | 2.9 | 2.9 | 3.3 | 4.4 | 4.3 | 5.8 |

* Burned to the end.

*(Continued on next page)*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Q.M.C. #27, Fabric #2 | 39.9 | Afterflame, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 0 | — | — | 2 | 4 | 4 |
| | | Char Area, in² | 3.6 | — | — | 3.4 | 3.4 | 2.5 |
| C.W.S.-Edgewood Fabric #1 | 38 | Afterflame, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 10 | — | — | 0 | 0 | 0 |
| | | Char Area, in² | 4.5 | — | — | 4.3 | 4.6 | 2.8 |
| C.W.S.-Edgewood Fabric #2 | 37 | Afterflame, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 0 | — | — | 17 | 29 | 1 |
| | | Char Area, in² | 3.6 | — | — | 3.2 | 2.8 | 2.6 |
| *Emulsion Treatments* | | | | | | | | |
| Q.M.C. #27, Fabric #3 | 32.6 | Afterflame, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 5 | — | — | 4 | 4 | 4 |
| | | Char Area, in² | 3.0 | — | — | 3.3 | 3.2 | 2.7 |
| *Urea-Phosphate Type Treatments* | | | | | | | | |
| Commercial Product R | 20 | Afterflame, sec. | 0 | 0 | 3 | 3 | 54 | — |
| | | Afterglow, sec. | 0 | 0 | 0 | 0 | 0 | — |
| | | Char Area, in² | 1.9 | 2.6 | 3.6 | 3.4 | C.B.** | — |
| Commercial Product M-1 | 16 | Afterflame, sec. | 0 | 0 | 0 | 0 | 1 | 22 |
| | | Afterglow, sec. | 0 | 0 | 0 | 0 | 0 | 0 |
| | | Char Area, in² | 4.0 | 4.0 | 4.0 | 2.3 | 2.2 | 7.0 |
| Q.M.C. #27, Fabric #4 | 16.7 | Afterflame, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Char Area, in² | 3.0 | — | — | 2.8 | 2.3 | 2.1 |
| Commercial Product M-3 | 23.9 | Afterflame, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Afterglow, sec. | 0 | — | — | 0 | 0 | 0 |
| | | Char Area, in² | 2.1 | — | — | 2.3 | 2.4 | 2.8 |

** Completely burned.

ness achieved are exemplified by Q.M.C. #27 fabric #4 and commercial product M-3. As will be discussed in the following pages, the application of these processes produces an appreciable loss in the tensile strength of the fabric and the addition of formaldehyde or reduction in the time or temperature of cure in order to minimize the tendering also lessens the permanence of the flameproofness obtained as shown in the cases of commercial products R and M-1.

**Effect on Desirable Textile Properties: Hand.** As in the case of the temporary flameproofing agents, the initial estimate of the efficacy of a durable treatment obtained by means of a preliminary evaluation of flameproofness and permanence must be supplemented by a more complete investigation of the effects of the treatment on the other desirable fabric characteristics. The high add-ons required by the double-bath and antimony oxide-chlorinated wax type of process exert a much more noticeable influence upon the hand of the treated fabric than was the case with the water-soluble retardants where the add-ons were in the order of 10–15%. In all cases, the treatment imparts appreciable stiffness to the fabric and the pigment components tend to produce a harsh and irritating surface. The stiffening effect of the resin or wax can be moderated by the addition of plasticizing agents and the fabric further softened by means of standard fabric finishing practices. The addition of a plasticizer or the partial substitution of a low chlorine-content chlorinated paraffin for one of higher chlorine content reduces the harshness and improves the flexibility of the fabric but often imparts an oily consistency to the surface. By varying the ingredients in this manner the finisher has considerable latitude in the nature of the finished fabric surface. Whether or not this type of treatment is acceptable for a given application is dependent upon the requirement set up and in the case of clothing fabrics for Army use must be determined by means of practical wear tests. In contrast, the urea-phosphate treated fabrics can be effectively flameproofed with much lower add-ons of retardant and the hand characteristics of the treated materials do not differ appreciably from those of the untreated fabric.

**Resistance to Moisture Vapor Transfer.** It might be expected that high additions of insoluble materials to a fabric would appreciably increase the resistance of that fabric to the passage of moisture vapor. The intrinsic resistances of the durably treated fabrics being considered are presented in Table 9 as determined by means of laboratory tests. It is at once apparent that the permeability of the fabric is not solely dependent upon the amount of added material, but is also a function of the physical nature of the finish. With purely inorganic materials, as illustrated by Q.M.C. #27 fabric #1, considerable amounts of the retardant may be added without appreciably increasing the resistance to moisture vapor transfer. When the mixture applied includes a film-forming resin or any other material which tends to block the interstices of the fabric, the permeability is significantly reduced. Of the fabrics listed, only three exhibit a striking in-

Table 9. Effect of Flameproofing Treatment Upon the Moisture Vapor Permeability of the Fabric

| Fabric | Add-On % | Intrinsic Resistance equiv. cm. of still air | % Increase in Resistance |
|---|---|---|---|
| 8.5 oz. Herringbone Twill, untreated | 0 | 0.14 | — |
| *Double Bath Treatments* | | | |
| Q.M.C. #27, Fabric #1 | 49 | 0.17 | 21 |
| Commercial Product Q | 29 | 1.18 | 740 |
| *Solvent Suspension Treatments* | | | |
| Commercial Product O | 65 | 0.49 | 250 |
| Commercial Product N | 35 | 0.19 | 36 |
| Q.M.C. #27, Fabric #2 | 40 | 0.44 | 215 |
| C.W.S.-Edgewood, Fabric #1 | 38 | 0.18 | 29 |
| C.W.S.-Edgewood, Fabric #2 | 37 | 0.18 | 29 |
| *Emulsion Treatments* | | | |
| Q.M.C. #27, Fabric #3 | 33 | 0.21 | 50 |
| *Urea-Phosphate Type Treatments* | | | |
| Commercial Product R | 16 | 0.19 | 36 |
| Commercial Product M-1 | 16 | 0.19 | 36 |
| Q.M.C. #27, Fabric #4 | 16 | 0.13 | 0 |
| Commercial Product M-3 | 24 | 0.13 | 0 |

crease in resistance: commercial product Q, product O and Fabric #2 from the Columbia project. The exceedingly high resistance of the zinc borate double-bath treatment may be attributable to a heavy deposit of zinc stearate which is allowed to remain on the fabric. The differences which are apparent between the various solvent-suspension fabrics might be due to variations in the nature of the chlorinated body employed. This is suggested by a comparison of fabrics 2 and 3 from the Q.M.C. #27 laboratories. In the case of the solvent suspension treatment, where Vinylite is used as the source of hydrogen chloride, the resistance is very great, whereas the emulsion which is very similar in composition with the exception of a substitution of chlorinated paraffin for the vinyl chloride resin, does not have a pronounced effect. The urea-phosphate type treatments, as might be expected on the basis of their method of fixation in the fabric, do not appreciably influence the moisture vapor permeability. Just what intrinsic resistance obtained by this laboratory test method would indicate a fabric likely to impose an excessive heat load upon the wearer would have to be determined by an extensive correlation with practical heat load experiments such as those discussed in a later section of this chapter. It is fairly certain, however, that the three fabrics which show an increase of 200% or more in their resistance to moisture vapor would be extremely uncomfortable under the stringent conditions of military operations where the men tend to perspire profusely.

**Fabric Strength.** With the exception of the urea-phosphate type, the durable flameproofing treatments do not produce any loss in the tensile

strength of the fabric as a result of the impregnation process. On the contrary, as shown in Table 10, the cohesion of the fibers produced by the

Table 10. Effect of Flameproofing Treatment Upon Fabric Strength
*(1-inch Raveled Strip Tensile Test)*

| Fabric | Warp Tensile Strength Untreated Fabric lbs./in. width | Warp Tensile Strength Treated Fabric lbs./in. width | % Change in Tensile Strength |
|---|---|---|---|
| *Double Bath Treatments* | | | |
| Commercial Product Q | 109 | 123 | + 13 |
| *Solvent Suspension Treatments* | | | |
| C.W.S.-M.I.T. Fabric | 110 | 104 | − 5 |
| Commercial Product O | 92 | 116 | + 26 |
| Commercial Product P | 92 | 120 | + 30 |
| Commercial Product N | 108 | 118 | + 9 |
| Q.M.C. #27, Fabric #2 | 110 | 148 | + 35 |
| C.W.S.-Edgewood, Fabric #1 | 112 | 124 | + 11 |
| C.W.S.-Edgewood, Fabric #2 | 112 | 119 | + 6 |
| *Emulsion Treatments* | | | |
| Q.M.C. #27, Fabric #3 | 112 | 129 | + 15 |
| *Urea-Phosphate Type Treatments* | | | |
| Commercial Product R | 130 | 96 | − 26 |
| Commercial Product M-1 | 100 | 88 | − 12 |
| Q.M.C.#27, Fabric #4 | 110 | 70 | − 36 |
| Commercial Product M-3 | 131 | 88 | − 33 |

binders employed generally results in a slight tensile increase. It should be borne in mind, however, that the fixation of the threads by the application of a resinous coating often greatly impairs the tear strength of a fabric. It is regretted that a comparable set of tear strength measurements was not available on these fabrics to supplement the tensile strength data presented. In the case of the fabrics treated with processes of the urea-phosphate type the tensile strength is appreciably impaired by the flameproofing treatment. The strength loss may range from 10 to 50% depending upon the nature of the compounds employed in the treating mixture and the time and temperature employed in curing. The variables which exist in the impregnating and curing processes have been thoroughly discussed in the preceding chapter. It was shown that the reduction in strength can be lessened appreciably by changes in the conditions of treating but that the better fabric strength is generally offset by a reduction in the permanence of the retardancy or an increase in the add-on required.

**Resistance to Laundering.** Since in the course of normal service, durably flameproofed fabrics are apt to encounter laundering conditions of various types, a complete evaluation of the relative suitability of the permanent treatments includes laundering in detergent solutions of varying alkalinity. The results of a series of laundering experiments on the solvent suspension, emulsion and urea-phosphate type treatments are summarized in Table 11. The antimony oxide-chlorinated body treatments

Table 11. Resistance of Durable Flameproofing Treatments to Laundering

| Fabric | Detergent Solution | pH | No. of Launderings | 45°-Microburner Flame Test: Afterflame sec. | 45°-Microburner Flame Test: Afterglow sec. | 45°-Microburner Flame Test: Char Area in² | Vertical Bunsen Flame Test: Afterflame sec. | Vertical Bunsen Flame Test: Afterglow sec. | Vertical Bunsen Flame Test: Char Length in. |
|---|---|---|---|---|---|---|---|---|---|
| Q.M.C. #27, Fabric #2; (Solvent Suspension) | 0.5% Igepon-T | 7.1 | 0 | 0 | 0 | 3.6 | 0 | 19 | 4.7 |
| | | | 1 | 0 | 10 | 3.2 | 0 | 20 | 5.0 |
| | | | 3 | 0 | 23 | 3.3 | 0 | 58 | 4.5 |
| | | | 6 | 0 | 70 | 2.8 | 0 | > 100 | 5.5 |
| | 0.5% G.I. Soap | 9.7 | 1 | 0 | 2 | 3.4 | 0 | 31 | 4.0 |
| | | | 3 | 0 | 4 | 3.4 | 0 | > 100 | 4.2 |
| | | | 6 | 0 | 4 | 2.5 | 0 | > 100 | 4.0 |
| | 0.5% G.I. Soap + 0.2% $Na_2CO_3$ | 10.4 | 1 | 0 | 3 | 3.7 | 0 | 30 | 4.9 |
| | | | 3 | 0 | 12 | 3.3 | 0 | 59 | 4.5 |
| | | | 6 | 0 | > 100 | 3.6 | 0 | > 100 | 4.9 |
| Q.M.C. #27, Fabric #3; (Emulsion) | 0.5% Igepon-T | 7.1 | 0 | 0 | 5 | 3.0 | 0 | 5 | 3.2 |
| | | | 1 | 0 | 5 | 3.0 | 0 | 7 | 4.0 |
| | | | 3 | 0 | 5 | 3.5 | 0 | 17 | 4.0 |
| | | | 6 | 0 | 5 | 3.7 | 0 | > 100 | 4.9 |
| | 0.5% G.I. Soap | 9.7 | 1 | 0 | 4 | 3.3 | 0 | 51 | 3.7 |
| | | | 3 | 0 | 4 | 3.2 | 0 | 46 | 3.2 |
| | | | 6 | 0 | 4 | 2.7 | 0 | 43 | 3.7 |
| | 0.5% G.I. Soap + 0.2% $Na_2CO_3$ | 10.4 | 1 | 0 | 3 | 3.3 | 0 | 51 | 3.7 |
| | | | 3 | 0 | 2 | 3.0 | 0 | 79 | 3.5 |
| | | | 6 | 0 | 5 | 3.1 | 0 | > 100 | 3.9 |
| Commercial Product M-3 | 0.5% Igepon-T | 7.1 | 0 | 0 | 0 | 2.1 | 0 | 0 | 2.4 |
| | | | 6 | 0 | 2 | 2.9 | 0 | 2 | 4.2 |
| | 0.5% G.I. Soap | 9.7 | 1 | 0 | 0 | 2.3 | 0 | 2 | 2.5 |
| | | | 3 | 0 | 2 | 2.4 | 0 | 2 | 3.1 |
| | | | 6 | 0 | 2 | 2.8 | 0 | 2 | 3.7 |
| | 0.5% G.I. Soap + 0.2% $Na_2CO_3$ | 10.4 | 6 | 31 | 0 | B.E.* | 0 | 5 | 3.5 |

* B.E.—Burned to the end.

are capable of withstanding six washes in any of the soap solutions employed without any apparent loss in the resistance to afterflaming. When correctly formulated it is immaterial whether the constitutents have been applied in the form of an emulsion or as a solvent suspension. In both cases, however, the resistance to afterglow is reduced, particularly in strongly alkaline detergent solutions, though in no case does the afterglow even approach that of the similar treatments which contain no glow-resistant ingredient. The urea-phosphate type of treatment is equally capable of withstanding six or more washes in neutral detergents or mildly alkaline soaps but is reduced in flameproofness when strongly alkaline soaps are employed. This is compatible with the nature of the fixation of the phosphate as discussed in previous chapters. As has been pointed out previously this type of treatment could be made resistant to six or more launderings in strongly alkaline soap but only with a corresponding increase in add-on or decrease in the strength of the treated fabric.

**Resistance to Ion-Exchange.** The resistance of the several types of durable treatments to immersion in synthetic "ocean water" is shown in Table 12. All of the better permanent type fabrics are capable of resisting

Table 12. Resistance of Durable Flameproofing Treatments to Sea Water Leaching
*(45°-Microburner Flame Test)*

| Fabric | Add-On % | Time of Rotation in Sea Water min. | Afterflame sec. | Afterglow sec. | Char Area in² |
|---|---|---|---|---|---|
| Commercial Product Q | 29 | 0 | 0 | 2 | 3.9 |
| (Double Bath) | | 120 | 0 | 1 | 3.4 |
| Q.M.C. #27, Fabric #2 | 40 | 0 | 0 | 0 | 3.5 |
| (Solvent Suspension) | | 120 | 0 | 10 | 2.9 |
| Q.M.C. #27, Fabric #3 | 33 | 0 | 0 | 5 | 3.0 |
| (Emulsion) | | 120 | 0 | 6 | 3.2 |
| Q.M.C. #27, Fabric #4 | 16 | 0 | 0 | 0 | 2.6 |
| (Urea-Phosphate Type) | | 120 | 0 | 0 | 3.7 |
| Commercial Product M-3 | 24 | 0 | 0 | 0 | 2.1 |
| (Urea-Phosphate Type) | | 120 | 0 | 0 | 3.0 |

the specified 120 minutes of exposure. In the case of the urea-phosphate type of fabric, this test is generally more severe than six standard launderings in either neutral detergents or 0.5% G.I. soap.

**Resistance to Weathering.** With flameproofed fabrics intended for outdoor usage, it is important that the treatment is not adversely affected by normal weathering conditions and particularly by ultraviolet irradiation. A series of outdoor exposure tests were set up with the emulsion, suspension and urea-phosphate type fabrics, and although the experiments had to be terminated much sooner than was intended, the data obtained, as presented in Table 13, indicate that exposure of these treated fabrics to

Table 13. Resistance of Durable Flameproofing Treatments to Weathering

| Fabric | Time | Tensile lbs./in. (warp/grab) | 45° Flame Test After-flame sec. | 45° Flame Test After-glow sec. | 45° Flame Test Char Area in² | Vertical Flame Test After-flame sec. | Vertical Flame Test After-glow sec. | Vertical Flame Test Char Length in. |
|---|---|---|---|---|---|---|---|---|
| *Outdoor Weathering, Normal East Coast Fall Weather* | | | | | | | | |
| Q.M.C. #27, Fabric #2 (Solvent Suspension) | 0 wks. | 192 | 0 | 0 | 2.2 | 0 | 15 | 4.1 |
| | 2 " | 191 | 0 | 1 | 2.8 | 0 | 14 | 3.7 |
| | 4 " | 202 | 0 | 0 | 2.6 | 0 | 21 | 4.2 |
| | 6 " | 197 | 0 | 0 | 2.7 | 0 | 17 | 4.0 |
| Q.M.C. #27, Fabric #3 (Emulsion) | 0 " | 166 | 0 | 3 | 2.1 | 0 | 4 | 3.0 |
| | 2 " | 170 | 0 | 0 | 2.3 | 0 | 3 | 3.2 |
| | 4 " | 168 | 0 | 0 | 1.7 | 0 | 8 | 3.4 |
| | 8 " | 164 | 0 | 4 | 2.8 | 0 | 12 | 3.0 |
| Commercial Product M-3 (Urea-Phosphate Type) | 0 " | 112 | 0 | 1 | 2.1 | 0 | 1 | 2.4 |
| | 2 " | 114 | 0 | 2 | 2.2 | 0 | 1 | 2.2 |
| | 4 " | 112 | 0 | 0 | 1.5 | 0 | 2 | 2.6 |
| | 8 " | 107 | 0 | 2 | 2.1 | 0 | 2 | 3.0 |
| *Accelerated Weathering (Atlas Weatherometer)* | | | | | | | | |
| Q.M.C. #27, Fabric #3 (Emulsion) | 0 hrs. | 163 | 0 | 3 | 2.1 | 0 | 4 | 3.0 |
| | 180 " | 160 | 0 | 4 | 3.0 | 0 | 15 | 5.0 |

normal weathering does not have any appreciable effect upon their flameproof qualities. The loss of fabric strength which has commonly been associated with the irradiation of fabrics treated with the chlorinated wax mixtures was not apparent, at least in the course of these admittedly short-term experiments. In support of this, the standard 180-hour exposure in the double arc Atlas Weatherometer did not produce any appreciable change in either the flameproofness or strength of fabric treated with the antimony oxide-chlorinated paraffin emulsion.

**Factors Influencing Selection.** In making a selection from among the available flameproofing treatments for processing Army clothing many different factors must be considered. If it is desired that the flameproofing process be adaptable to field impregnation, the choice is limited to some of the metallic oxide-chlorinated body suspensions or the water-soluble retardants. The former have the advantage of permanence but also possess the disadvantages of being rather difficult to apply in the field, producing a garment of rather unsightly appearance and requiring excessive add-ons of 30% or more. The latter will be completely destroyed by rain, immersion or even profuse perspiration but are attractive because of the ease with which they may be applied and the low add-ons required for effective flameproofing. Finally, the water-soluble treatments in general will not inconvenience the wearer in any way whereas the pigment processes may add to the heat load of the garment. Of the water-soluble flameproofing agents considered in this section, any one of the five or six better retardants would be nearly equally satisfactory.

If it is intended that the fabric be processed in the form of yard goods prior to fabrication of the garments, the treatment selected would probably be one of the durable type. Of this group the outstanding example is the urea-phosphate type of treatment. The treated fabric in this case possesses excellent resistance to both afterflaming and afterglow and is capable of retaining these flameproof characteristics throughout prolonged leaching, laundering or exposure to the weather. The application of the retardant process does not adversely influence the hand of the fabric or its permeability to moisture vapor. Finally the amount of flameproofing agent required for effective retardancy is nearly as low as with the temporary treatments. The one serious drawback to this process is the appreciable strength loss encountered in the course of the treating procedure. By compromising the loss in fabric strength, however, with the permanence of the flameproofness achieved it is very possible that a treated fabric could be obtained which would be acceptable for military clothing purposes. The antimony oxide-chlorinated wax treatments, on the other hand, do not cause any reduction in the strength of the fabric and can be formulated to produce a high degree of flameproofness which is also resistant to leaching and laundering. They suffer from the disadvantage of high add-on and also generally adversely affect the hand of the fabric and its moisture vapor permeability. Furthermore, the resistance to afterglow is rarely complete and is generally reduced by laundering.

In determining which of these types of treatment would be preferable for use in military clothing, the decision must be based upon practical wearing tests, in which human subjects are clothed in the flameproofed garments and subjected to normal and accelerated conditions intended to simulate the stress of military operations. In the course of these large-scale experiments, the treated fabrics would be tested for their performance as to flameproofness, strength and durability and for their influence upon the wearer both with respect to comfort or heat load and any possible toxicological symptoms which they might produce. The results of practical wearing tests of this type are considered in the following pages.

## 2. Performance Evaluations

*E. Folger Taylor and William R. Christensen*

To supplement the preceding laboratory experiments, extensive practical evaluations of several flameproof finishes were carried out at the Climatic Research Laboratory, Lawrence, Massachusetts, and at the Quartermaster Board, Camp Lee, Virginia. The tests conducted by the Climatic Research Laboratory will be discussed first.

These experiments were designed to investigate the effects of ordinary wear and laundering, exposure to rainfall, profuse perspiration, sea water

immersion and stockroom storage on the flame retardancy and strength of flameproofed uniforms. Three differently treated sets of garments were used which will be referred to as Types 1, 2 and 3. In order to avoid cumbersome repetition in the following sections on performance and physiological evaluations, this classification by type numbers will be adhered to. The three treatments studied may be briefly described as follows:

The Type 1 garments consisted of an 8.5 oz. herringbone twill fabric, dyed olive drab No. 7, constructed into two-piece work suits and then impregnated with a mixture of borax, boric acid and diammonium hydrogen phosphate in the ratio of 7:3:5. Prior to impregnation, the garments were laundered to remove excess sizing and increase absorbency in order that an adequate and uniform pickup of retardant could be obtained. The impregnation process was conducted in the washwheel of a mobile laundry.[1] The concentration of the solution and the time of extraction were adjusted so as to leave the desired add-on of approximately 12%. This is slightly above the minimum effective add-on previously determined. The exact add-on actually obtained was determined by weighing conditioned garments before and after impregnation. With this method of application, the treatment was more or less spotty, an excess of crystalline salts accumulating in certain sections of the garments and causing stiffening and a rough, undesirable hand. Other sections of the same garments received sub-optimal impregnations.

Type 2 garments were constructed of 8.5 oz. herringbone twill, dyed olive drab No. 7 which had been previously flameproofed in yard goods form by a commercial urea-phosphate type treatment similar to that described in Chapter V, Section B–1. The total add-on was 16–20% and the finish had little effect on the appearance, flexibility and hand of the material, although the tensile strength was significantly reduced.

The third set of uniforms tested, which have been designated as Type 3, were also impregnated in yard goods form according to the antimony oxide-vinyl resin process developed at the Chemical Warfare Service Development Laboratory at the Massachusetts Institute of Technology. The base fabric again was an 8.5 oz. herringbone twill dyed olive drab No. 7. As a result of impregnation, the cloth became quite stiff and required considerable finishing treatment before it was usable in garment form. With this type of flameproofing process, the physical properties of the finished fabric are greatly dependent upon the nature and extent of the finishing operations employed. This variable has given rise to appreciable differences in hand and absorbency from one mill run to another.

The flameproof characteristics of the three treated fabrics were studied by means of both the Vertical-Bunsen and 45°-Microburner flame tests.[2] For this discussion, only the results of the 45° test have been presented

[1] See Chapter V, Section A–2.

[2] See Chapter IV, Section B–2 for details of test procedure.

and these are recorded in terms of the time of afterflaming in seconds, time of afterglow in seconds, and char area in square inches. Breaking strength measurements of the treated fabrics were made by means of the 1-inch raveled strip test using a Scott Tensile Tester.[3] In all cases the sample garments were conditioned in the standard atmosphere of 70° F. and 65% R.H. for at least 24 hours before being cut into specimens and tested.

One of the most troublesome problems in establishing the test methods for these practical studies was the selection of proper sampling techniques. Experimentation resulted in taking representative samples as shown in Figure 18, Chapter IV. With each uniform five square specimens were taken for the 45°-Microburner flame test, five oblong specimens for the Vertical-Bunsen flame test, and eight strips for the tensile strength measurement. The locations selected for cutting specimens were believed to be those which would cover the range of possible effects resulting from wear, sweat, soiling, etc. When specimens were to be tested before and after laundering, control was maintained by taking the "before" and "after" specimens from the same general location but on the other half of the garment.

To serve as a basis of comparison with all subsequent tests, control values of the flame test and tensile test data were obtained for each of the three types of uniforms. These were determined on new, unworn garments averaging at least ten individual observations in each case. The tensile strength of the Type 1 uniforms can serve as a basis of comparison to determine the extent of the tensile loss caused by the urea-phosphate type treatment and the tensile gain induced by the vinyl resin treatment.

### a. Wear and Laundering

In testing the resistance of the flameproofed uniforms to normal wear and laundering, six uniforms of each of the three types were subjected first to similar wear conditions for a period of one week, sampled and tested. Each garment was then laundered using the detergent solution specified for the type of treatment, resampled and again tested for flameproofness and fabric strength. Thus, the data collected afforded an estimate of the effects of laundering as well as the effects of wear. Some difficulty was encountered in selecting the best method for conducting these experiments. Since three types of uniforms were being considered, the most accurate control of individual variations could be obtained by having six subjects wear the uniforms on successive weeks. Such a procedure, however, would have invited the criticism that weather conditions had not been controlled. As earlier work had demonstrated the serious effect of sweating upon the Type 1 uniform, it was considered preferable to control the climatic con-

[3] See Chapter IV, Section B-3 for details of test procedure.

ditions rather than the subjects. Consequently, eighteen soldiers, all performing approximately the same type of work, were selected as experimental subjects. In this manner the three types of garments could be tested concurrently under identical environmental conditions. The conditions under which the uniforms were worn cannot be described as simulating field wear since all subjects were engaged in laboratory work. The uniforms were worn constantly but were not subjected to mud, rain, abrasion by crawling, etc. They were in use, however, for at least eight hours during each day. The launderings at the end of the first week's wear were performed in a standard Quartermaster Corps mobile laundry according to the following schedule for cotton clothing:

| Operation | Supplies | Time (min.) | Water Level (inches) | Temperature °F. |
|---|---|---|---|---|
| 1 Suds | Detergent | 5 | 6 | 100 |
| 2 Suds | Detergent | 5 | 4 | 140 |
| 3 Rinse | None | 3 | 8 | 140 |
| 4 Rinse | None | 3 | 8 | 120 |
| 5 Rinse | Sour | 3 | 8 | 100 |

Tumbler dried at 245 ± 10° F.

The detergent solutions used in the sudsing operations were as follows:

| Uniform | Laundering Solution Percentage Concentration | Item |
|---|---|---|
| Type 1 | 0.5 | Igepon-T |
| Type 2 | 0.5 | Chip Soap |
| | 0.2 | $Na_2CO_3$ |
| Type 3 | 0.5 | Chip Soap |
| | 0.2 | $Na_2CO_3$ |

Following the one-week wear period, the Type 1 garments were eliminated from the test, since the temporary treatment was completely removed by a single laundering, and six uniforms of each of the remaining two types were subjected to three additional weeks of wear with a laundering at the end of each week. Wearing conditions were the same as previously described but the detergent solutions in the laundering process were changed to the following:

| Uniform | Laundering Solution Percentage Concentration | Item |
|---|---|---|
| Type 2 | 0.5 | Chip Soap |
| Type 3 | 0.5 | Chip Soap |
| | 0.2 | $Na_2CO_3$ |

Sampling and testing of garments was performed before and after the third wash, *i.e.* after 3 weeks' wear and 2 launderings and after 3 weeks' wear and 3 launderings.

Continuing the experiment, other Type 2 and 3 uniforms were worn for an additional 3 weeks and tested according to the previously described techniques after 6 weeks' wear and 5 launderings and again after the sixth laundering. The conditions of wear were the same as for the previous tests, but the detergent solutions used in laundering were altered as follows:

| Uniform | Laundering Solution Percentage Concentration | Item |
|---|---|---|
| Type 2 | 0.5 | Igepon-T |
| Type 3 | 0.5 | Chip Soap |
| | 0.2 | $Na_2CO_3$ |

The preliminary tests after the sixth week indicated that the Type 2 uniforms still retained the majority of their original flameproof properties. Therefore, three of the test garments were continued for an additional 3-week period, making a total of 9 weeks of wear and 9 launderings. The Type 3 garments were not continued beyónd the 6-week period because of the highly excessive afterglow which was felt to be undesirable in clothing and because of the subjective undesirability of this finish. The tests on Type 2 uniforms were stopped at the end of 9 weeks since the garments showed definite signs of wear at that time.

The results of the tests on Type 1 garments are summarized in Table 14 along with the control values obtained with the unworn uniforms. It is apparent that this treatment was appreciably impaired by the relatively mild wear conditions described. Those areas which were subjected to the greatest abrasion and the maximum sweat formation were most seriously affected. When one considers that these uniforms were exposed to only the mildest conditions of use and environment, it is apparent that their performance was unsatisfactory. In no case were they exposed to rain, mud, excessive perspiration or wear and abrasion of a severity approaching combat conditions, yet excessive afterflame and afterglow occurred in several specimens. None of the flameproof properties were retained after the single laundering. In considering the tensile strength data it should be emphasized that the figures shown represent the average of 48 separate measurements, 8 on each of 6 uniforms. In comparing the values before and after laundering with those of the unworn control garments it is obvious that the strength of the fabric in the Type 1 uniforms was not affected by the one week's wear nor by the single laundering.

The data obtained with the Type 2 uniforms throughout the 9-week wear period is summarized in Table 15, again including control values on unworn uniforms as a basis of comparison. In this case the initially adequate flameproof qualities were retained throughout a 3-week wear period with a laundering at the end of each week. The time of afterflame and afterglow remained zero in all cases although the slight increase in

Table 14. Performance of Type 1 Flameproofed Uniforms on Exposure to Wear and Laundering

*(45°-Microburner Flame Test; 1-inch Raveled Strip Tensile Test)*

| | | Jacket | | | | | | | | | Trousers | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | | |
| Weeks of Wear | No. of Launderings | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | Mean Tensile Strength lbs./in. |
| 0 | 0 | — | – | — | — | – | — | — | – | — | — | – | — | — | – | — | 0* | 0 | 2.4 | 99 |
| 1 | 0 | 11 | 7 | 3.4 | 2 | 1 | 2.0 | 3 | 0 | 2.3 | 2 | 4 | 2.2 | 4 | 6 | 2.6 | 4 | 4 | 2.5 | 101.5 |
| 1 | 1 | 45 | – | — | 45 | – | — | 46 | – | — | 44 | – | — | 43 | – | — | 45** | – | — | 103.9 |

* The majority of these values were zero. However, because of uneven impregnation, occasional specimens showed definite afterflaming, the time varying from 2 to 36 seconds.

** All specimens were completely consumed by afterflaming and afterglow was in excess of 100 seconds in all cases.

Table 15. Performance of Type 2 Flameproofed Uniforms on Exposure to Wear and Laundering

*(45°-Microburner Flame Test; 1-inch Raveled Strip Tensile Test)*

| | | Jacket | | | | | | | | | Trousers | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | | |
| Weeks of Wear | No. of Launderings | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | Mean Tensile Strength lbs./in. |
| 0 | 0 | — | – | — | — | – | — | — | – | — | — | – | — | — | – | — | 0 | 0 | 2.5 | 84.0* |
| 1 | 0 | 0 | 0 | 2.2 | 0 | 0 | 2.1 | 0 | 0 | 2.0 | 0 | 0 | 2.1 | 0 | 0 | 2.2 | 0 | 0 | 2.1 | 88.8 |
| 1 | 1 | 0 | 0 | 2.2 | 0 | 0 | 2.2 | 0 | 0 | 2.2 | 0 | 0 | 2.0 | 0 | 0 | 2.0 | 0 | 0 | 2.1 | 84.4 |
| 3 | 2 | 0 | 0 | 2.2 | 0 | 0 | 2.4 | 0 | 0 | 2.6 | 0 | 0 | 2.7 | 0 | 0 | 2.4 | 0 | 0 | 2.5 | 86.8 |
| 3 | 3 | 0 | 0 | 2.2 | 0 | 0 | 2.2 | 0 | 0 | 2.3 | 0 | 0 | 2.3 | 0 | 0 | 2.4 | 0 | 0 | 2.3 | 84.5 |
| 6 | 5 | 0 | 1 | 2.9 | 0 | 1 | 3.0 | 0 | 1 | 3.2 | 0 | 1 | 3.1 | 0 | 1 | 3.1 | 0 | 1 | 3.0 | 79.8 |
| 6 | 6 | 0 | 1 | 3.1 | 0 | 1 | 3.0 | 0 | 1 | 5.3 | 0 | 1 | 2.9 | 0 | 2 | 2.9 | 0 | 1 | 3.4 | 77.0 |
| 9 | 8 | 17 | 0 | 7.0 | 1 | 0 | 3.8 | 9 | 0 | 5.2 | 14 | 0 | 6.5 | 31 | 0 | 9.3 | 15 | 0 | 6.4 | 54.0 |
| 9 | 9 | 10 | 0 | 5.6 | 11 | 0 | 5.2 | 15 | 0 | 6.6 | 27 | 0 | 9.3 | 21 | 0 | 8.8 | 17 | 0 | 7.1 | 50.0 |

* Two distinct groups of uniforms were used in this test, one having high and the other low tensile strength. This value represents a random sampling of both groups.

char area would suggest that the efficiency had begun to be slightly impaired. At the end of the sixth week, the resistance to afterflame and afterglow was not significantly lower than the unworn control specimens but the rapidly increasing char area now indicated a significant effect upon the efficiency of the treatment. This trend is substantiated by the results obtained after 9 weeks of wear and 8 launderings. The test specimens now exhibited appreciable afterflaming and char areas approximately three times as great as the control values. The final laundering at the end of the ninth week added to the extent to which the efficiency of the treatment had been reduced. Apparently the urea-phosphate type of treatment was only slowly impaired by wear and laundering up to a certain critical point, beyond which the deterioration became much more rapid.

The interpretation of the tensile strength data in Table 15 is subject to some uncertainty. It appears that two different base fabrics were involved: one having a tensile strength of approximately 100 lbs./in. after treatment and the other approximately 80 lbs./in. For this reason it is hazardous to make a definite statement as to the effect of wear upon the fabric. It is possible that in some cases the tensile values may have been influenced to a greater extent by the proportion of the two types of fabric in the specimens selected than by the wear and launderings to which the garments had been exposed. Indications are that the fabric strength was affected similarly to the flame resistance. The strength was relatively unaffected by the first 3 weeks of wear and laundering but was somewhat reduced in the course of the next 3-week period. The further reduction which occurred in the 6- to 9-week period was much more severe, indicating again that a critical point had been passed. In each case the laundering treatments caused a slight but noticeable lowering of the tensile strength, amounting to from 2 to 4 lbs./in.

When the Type 2 uniforms were examined at the conclusion of the 9-week test period, two pairs of trousers demonstrated evidence of severe wear. Threadbare patches had appeared at the knees and seat and the seams had begun to fail. Nevertheless, the conditions of the remainder of the garments appeared to be no worse than regular H.B.T. uniforms when worn under comparable conditions. It should be noted here also that the trousers which indicated severe wear were in the low tensile strength group of the two types of Type 2 uniforms.

The flame and tensile test data on the Type 3 uniforms are summarized in Table 16. The initial protection afforded by this antimony oxide-vinyl resin treatment was quite inferior to the Type 1 and Type 2 garments. The resistance to afterflaming was excellent but the fabric glowed even more severely than untreated H.B.T. This is felt to be highly undesirable in clothing fabrics as has been pointed out in previous chapters. The large char area which resulted can be attributed in great measure to the extensive deterioration caused by the afterglow. The initial flameproof char-

Table 16. Performance of Type 3 Flameproofed Uniforms on Exposure to Wear and Laundering

*(45°-Microburner Flame Test; 1-inch Raveled Strip Tensile Test)*

| | | Jacket | | | | | | | | | Trousers | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | | |
| Weeks of Wear | No. of Launderings | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | Mean Tensile Strength lbs./in. |
| 0 | 0 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | 0 | 624 | 5.2 | 120.0 |
| 1 | 0 | 0 | 827 | 8.4 | 0 | * | 4.2 | 0 | * | 4.1 | 0 | * | 4.2 | 0 | * | 3.5 | 0 | * | 4.0 | 122.6 |
| 1 | 1 | 0 | 843 | 10.1 | 0 | * | 4.6 | 0 | * | 5.1 | 0 | * | 3.7 | 0 | * | 3.7 | 0 | * | 4.3 | 115.8 |
| 3 | 2 | 1 | 916 | 12.7 | 1 | * | 5.0 | 1 | * | 5.3 | 1 | * | 5.5 | 1 | * | 5.6 | 1 | * | 5.4 | 103.1 |
| 3 | 3 | 0 | 919 | 13.8 | 0 | * | 6.1 | 0 | * | 5.7 | 0 | * | 5.4 | 0 | * | 4.5 | 0 | * | 5.4 | 103.5 |
| 6 | 5 | 0 | 873 | 14.5 | 0 | * | 5.6 | 0 | * | 5.9 | 1 | * | 5.5 | 0 | * | 5.5 | 0 | * | 5.6 | 93.6 |
| 6 | 6 | 1 | 814 | 15.4 | 2 | * | 5.8 | 0 | * | 5.7 | 0 | * | 5.3 | 0 | * | 5.5 | 1 | * | 5.5 | 96.4 |

* Afterglow in excess of 300 seconds.

acteristics of these uniforms were not appreciably affected, however, by 6 weeks' wear with an alkaline soap laundering at the end of each week. Considering only the shoulder specimens in Table 16, it does appear that the treatment was reduced somewhat in its effectiveness as evidenced by the increase in the size of the char area. The other char area figures cannot be similarly compared since, in many cases, afterglow was extinguished at the end of 300 seconds. The conclusions would be, on the basis of these data, that this particular flameproofing treatment was not significantly influenced by the wear and laundering experiments described. The excellent flame resistance was retained throughout 6 weeks of wear and 6 launderings but the highly excessive afterglow, which was prevalent in all specimens, precludes the approval of Type 3 uniforms for military clothing purposes.

The tensile strength of the Type 3 uniforms was progressively degraded by the wear and laundering procedures. The reduction was not apparent at the end of the first week of wear but became increasingly severe at the end of the 3- and 6-week periods. The final strength loss approximated 20% of that of the unworn control garments. The data available are not conclusive as to whether this loss was due to the wear or to the weekly launderings. The results of Table 16 indicate that it was more likely due to the former.

Since each subject wore only one type of uniform during the test period it was impossible to obtain any quantitative evaluation of the comparative subjective desirability of the three test items. Judging from the complaints of the men who wore Type 1 and Type 3 uniforms, however, these can be regarded as less satisfactory. There were no indications of serious irritations or any skin rash but the subjects continually complained about the rigidity, unpleasant hand and lack of ventilation in these two sets of uniforms. In contrast, there appeared to be no noticeable difference between the Type 2 garments and regular untreated fatigues. As the wear period progressed the subjects clad in the Type 3 garments reported a definite decrease in the stiffness and undesirability of the fabric. This appeared to be increasingly true as the garment was progressively worn and laundered.

Since the previous tests had shown that two different batches of cloth were used in preparing the Type 2 uniforms, a second series of wear and laundering studies were initiated in which this source of possible error was eliminated. Particular care was exercised in the selection of the test garments, ensuring that all items were of approximately equal tensile strength. On this basis it was also assumed that all garments chosen had been prepared in one mill run of cloth which had been flameproofed in a single operation. In this series of experiments, the procedures were similar to those previously described, with the exception that flame and tensile tests were carried out at 6-, 8-, 10- and 12-week periods. Furthermore, the weekly launderings were performed using 0.5% Igepon-T detergent.

Table 17. Performance of Type 2 Flameproofed Uniforms on Exposure to Wear and Laundering

*(45°-Microburner Flame Test; 1-inch Raveled Strip Tensile Test)*

| | | Jacket | | | | | | | | | Trousers | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | | |
| Weeks of Wear | No. of Launderings | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | Mean Tensile Strength lbs./in. |
| 0 | 0 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | — | 0 | 0 | 2.4 | 106 |
| 6 | 5 | 0 | 0 | 3.1 | 0 | 0 | 2.9 | 0 | 0 | 2.8 | 0 | 0 | 2.8 | 0 | 0 | 2.8 | 0 | 0 | 2.9 | 89 |
| 6 | 6 | 0 | 0 | 3.0 | 0 | 0 | 3.4 | 0 | 0 | 3.2 | 0 | 0 | 3.5 | 0 | 0 | 3.5 | 0 | 0 | 3.3 | 86 |
| 8 | 7 | 0 | 0 | 3.5 | 0 | 0 | 3.5 | 0 | 0 | 3.7 | 0 | 0 | 3.6 | 0 | 0 | 3.7 | 0 | 0 | 3.6 | 78 |
| 8 | 8 | 0 | 0 | 3.9 | 0 | 0 | 3.7 | 0 | 0 | 3.9 | 0 | 0 | 3.7 | 0 | 0 | 3.9 | 0 | 0 | 3.8 | 71 |
| 10 | 9 | 0 | 0 | 3.6 | 0 | 0 | 3.2 | 1 | 0 | 3.6 | 1 | 0 | 3.6 | 0 | 0 | 3.6 | 0 | 0 | 3.5 | 72 |
| 10 | 10 | 1 | 0 | 3.6 | 1 | 0 | 3.5 | 8 | 0 | 5.3 | 3 | 0 | 4.2 | 4 | 0 | 4.5 | 1 | 0 | 4.2 | 66 |
| 12 | 11* | 1 | 0 | 3.6 | 1 | 0 | 3.6 | 1 | 0 | 3.8 | 0 | 0 | 3.0 | 28 | 0 | 10.0 | — | — | — | 64 |
| | | 1 | 0 | 3.6 | 0 | 0 | 3.3 | 2 | 0 | 5.2 | 23 | 0 | 9.7 | 1 | 0 | 4.4 | — | — | — | 59 |
| | | 0 | 0 | 4.2 | 2 | 0 | 5.0 | 2 | 0 | 5.2 | 1 | 0 | 4.0 | 2 | 0 | 5.1 | — | — | — | 63 |
| | | 1 | 0 | 3.9 | 2 | 0 | 4.3 | 2 | 0 | 5.0 | 0 | 0 | 3.9 | 1 | 0 | 4.4 | — | — | — | 57 |
| | | 1 | 0 | 3.8 | 1 | 0 | 2.9 | 25 | 0 | 10.4 | 0 | 0 | 3.8 | 1 | 0 | 2.9 | — | — | — | 74 |
| 12 | 12* | 1 | 0 | 4.1 | 1 | 0 | 3.9 | 2 | 0 | 4.5 | 1 | 1 | 4.1 | 4 | 0 | 5.9 | — | — | — | 63 |
| | | 3 | 0 | 5.0 | 1 | 0 | 3.5 | 2 | 0 | 4.1 | 2 | 0 | 4.5 | 26 | 0 | 9.2 | — | — | — | 60 |
| | | 1 | 0 | 4.3 | 32 | 0 | 9.8 | 35 | 0 | 10.0 | 1 | 0 | 4.7 | 0 | 0 | 4.3 | — | — | — | 62 |
| | | 2 | 0 | 4.6 | 28 | 0 | 9.4 | 28 | 0 | 9.8 | 2 | 0 | 4.5 | 2 | 0 | 4.4 | — | — | — | 56 |
| | | 1 | 0 | 3.6 | 1 | 0 | 4.0 | 43 | 0 | 12.0 | 0 | 0 | 4.1 | 28 | 0 | 10.7 | — | — | — | 68 |

* Data for individual subjects is given because of the variability shown.

The results of this study are summarized in Table 17, including control values obtained by testing ten samples selected from representative unworn uniforms. The results of the 45°-Microburner flame test demonstrate the superior flameproof properties which the garments possessed initially and indicate that there was no appreciable reduction in these characteristics throughout 8 weeks of wear with weekly launderings in neutral detergent. The slight increase in char area, which appears to be progressive, indicates, however, that the effectiveness of the flameproofing treatment was being noticeably, though insignificantly, reduced. At the end of ten weeks of wear and nine launderings, the flame and glow resistance were still comparable to that of the original fabric. The tenth laundering, however, appeared to be on the borderline of incipient flaming. This loss of effectiveness was further accentuated by two additional weeks of wear and laundering. The 12-week specimens showed appreciable afterflaming in several instances and it would appear that the effective flameproofness of these garments had, by then, been practically destroyed. These results are in more or less agreement with those shown in Table 15.

The tensile strength of the unworn control garments in Table 17 well illustrates that this series of Type 2 garments had a relatively high initial tensile strength, 106 lbs./in. as compared with 84 lbs./in. in the first study. The drop in tensile strength with wear and laundering was rapid, however, reaching 86 lbs./in. after 6 weeks' wear and 6 launderings as compared with 77 lbs./in. after the same period in the earlier experiment. The decrease with additional wear periods was progressive, though the majority of the strength loss apparently occurred in the first few weeks. Since strength measurements were not made before and after laundering at the end of each week, it is difficult to attribute the decrease solely to either the wear or the washing. It is probable, based upon the nature of the urea-phosphate type of flameproofing composition, that the majority of the loss in retardancy was caused by the launderings rather than by any effects of the wear involved. In the case of fabric strength, however, the decrease observed is probably attributable to both the wear and laundering conditions. In any case, the severe loss in fabric strength which occurs in the process of applying the flameproofing treatment to the fabric and subsequent additional degradation resulting in the course of normal wear and laundering is a serious limitation of this type of treatment. The wearing characteristics of the urea-phosphate treated fabrics will have to be improved before they can be considered for any but special applications to military clothing which is, in time of combat, subject to severe wear.

#### b. Perspiration

In view of the scarcity of laboratory test data on the resistance of flameproofed fabrics to perspiration, it was desirable to include in these practi-

cal wear tests an estimation of the relative resistance of flameproofed uniforms to the action of profuse perspiration. Since the heat load experiments described in Section 3 consisted of exposures of human subjects to extreme temperature and humidity while clad in the flameproofed garments, no additional program was required for this study. The uniforms used in the heat load studies were also utilized in determining the effect of perspiration on the flameproof qualities and tensile strength of the fabric. Available records permitted precise calculation of the total wearing time under jungle conditions for each uniform and also the total quantity of perspiration lost by the subject during the period of exposure. Presumably the majority of the perspiration secreted was absorbed by the test garment. In the physiological heat load experiments two garments of each type were worn; one uniform was exposed to one 3-hour period and the other to two identical 3-hour periods. There were available, therefore, for this perspiration study two sets of test uniforms, one which had been worn for 3 hours at 90° F. and 85% R.H., and a second which had been worn for 6 hours under the same conditions and had been subjected to approximately twice as much perspiration. The sampling and testing of these garments was carried out as described in Section a. The results obtained with the three types of flameproofed uniforms are summarized in Table 18.

The subjects wearing the Type 1 uniforms produced an average of 1300 grams of sweat during the 3-hour period and approximately 2100 grams in the course of 6 hours of wear. It is apparent from the data that this amount of perspiration removed appreciable amounts of the water-soluble retardant from certain sections of the garment. In general the extent of the deterioration was proportional to the perspiration secreted. Considerable variability was apparent from one subject to the other due, no doubt, to the spottiness of the impregnation and the physiological variations among the subjects. This inconsistency is apparent in that some garments appear to have lost appreciable retardancy in regions which in other garments are relatively unaffected. Despite these differences, however, it is apparent that even 3 hours of wear under jungle conditions produced sufficient perspiration to leach out effective flame resistance with this type of treatment. Increasing the wearing time to 6 hours increased the severity of the loss of retardancy, particularly in the shoulder, seat and knee regions. The lower back and front sections of the jacket were relatively unaffected. It would seem, therefore, that a water-soluble, temporary flameproofing treatment, such as this 7:3:5 mixture, could not be considered satisfactory for clothing purposes in instances where atmospheric conditions produce profuse perspiration.

In the case of the Type 2 uniforms, the flameproofness was not noticeably affected by either 3 hours or 6 hours of wear under jungle conditions. The exposure to 900–1800 and 2500 grams of sweat respectively did not impair the retardancy of these garments; afterflame and afterglow were

Table 18. Effect of Profuse Perspiration on the Flameproofed Uniforms, Types 1, 2 and 3

(*45°-Microburner Flame Test*)

| | | Total | Jacket | | | | | | | | | Trousers | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | |
| Uniform | Hrs. of Wear (90° F.; 85% R.H.) | Sweat Produced gms. | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² |
| Type 1* | 3 | 1600 | 37 | 7 | 7.0 | 62 | 6 | 9.7 | 0 | 0 | 1.9 | 3 | 15 | 2.4 | 34 | 5 | 6.0 | – | — | — |
| | | 1500 | 0 | 9 | 2.5 | 0 | 1 | 2.3 | 0 | 1 | 2.1 | 2 | 12 | 2.1 | 0 | 17 | 2.2 | – | — | — |
| | | 1140 | 30 | 1 | 5.6 | 0 | 0 | 1.9 | 0 | 0 | 1.6 | 2 | 11 | 2.2 | 4 | 16 | 2.9 | – | — | — |
| | | 1530 | 43 | 98 | 9.8 | 0 | 0 | 1.6 | 0 | 0 | 1.4 | 5 | 23 | 2.1 | 28 | 12 | 2.7 | – | — | — |
| | | 1110 | 1 | 5 | 2.4 | 0 | 0 | 2.4 | 0 | 0 | 2.1 | 6 | 8 | 2.3 | 2 | 13 | 2.4 | – | — | — |
| | | 1030 | 30 | 3 | 7.1 | 1 | 0 | 2.0 | 0 | 0 | 2.2 | 33 | 33 | 6.9 | 30 | 68 | 9.7 | – | — | — |
| | | 1200 | 2 | 0 | 2.6 | 0 | 0 | 2.4 | 1 | 0 | 2.2 | 2 | 101 | 3.1 | 23 | 65 | 8.9 | – | — | — |
| | | 1510 | 1 | 12 | 3.1 | 6 | 9 | 1.7 | 2 | 0 | 2.1 | 3 | 12 | 2.4 | 3 | 11 | — | – | — | — |
| | | 1130 | 34 | 4 | 5.4 | 0 | 0 | 2.0 | 0 | 0 | 1.8 | 1 | 12 | 2.4 | 0 | 77 | 2.3 | – | — | — |
| | 6 | 3060 | 62 | 71 | 16.5 | 0 | 65 | 3.2 | 0 | 0 | 1.9 | 1 | 28 | 2.8 | 0 | 29 | 2.7 | – | — | — |
| | | 2880 | 41 | 155 | 13.0 | 0 | 0 | 1.8 | 0 | 0 | 2.0 | 5 | 98 | 3.6 | 44 | 63 | 9.7 | – | — | — |
| | | 1950 | 37 | 189 | 14.1 | 0 | 0 | 2.1 | | 1 | 2.5 | 0 | 14 | 2.8 | 1 | 18 | 2.2 | – | — | — |
| | | 1170 | 44 | 150 | 14.6 | 0 | 0 | 2.8 | 0 | 0 | 2.8 | 27 | 124 | 10.0 | 0 | 19 | 2.6 | – | — | — |
| | | 2240 | 23 | 165 | 9.9 | 0 | 0 | 2.1 | 0 | 0 | 2.7 | 2 | 0 | 3.1 | 15 | 82 | 5.8 | – | — | — |
| | | 2050 | 44 | 11 | 10.2 | 0 | 0 | 2.1 | 2 | 0 | 2.4 | 32 | 72 | 9.0 | 16 | 7 | 4.5 | – | — | — |
| | | 2370 | 29 | 130 | 14.0 | 0 | 7 | 2.2 | 0 | 6 | 2.3 | 10 | 84 | 3.3 | 30 | 30 | 4.2 | – | — | — |
| | | 2170 | 32 | 76 | 9.9 | 0 | 0 | 2.0 | 0 | 1 | 2.1 | 7 | 21 | 3.5 | 0 | 15 | 2.6 | – | — | — |
| | | 1500 | 70 | 63 | 15.7 | 0 | 0 | 2.1 | 1 | 0 | 2.4 | 2 | 23 | 2.7 | 1 | 14 | 2.4 | – | — | — |
| Type 2 | 3 | 1108 | 0 | 0 | 2.5 | 0 | 0 | 2.4 | 0 | 0 | 2.5 | 0 | 0 | 2.3 | 0 | 0 | 2.4 | 0 | 0 | 2.4 |
| | 6 | 2518 | 0 | 0 | 2.3 | 0 | 0 | 2.1 | 0 | 0 | 2.1 | 0 | 0 | 2.3 | 0 | 0 | 2.2 | 0 | 0 | 2.2 |
| Type 3 | 3 | 1173 | 0 | 937 | 12.5 | 0 | 908 | 11.1 | 0 | 815 | 7.8 | 0 | 868 | 7.7 | 0 | 853 | 8.1 | 0 | 876 | 9.4 |
| | 6 | 2154 | 0 | 890 | 11.0 | 0 | > 300 | 4.1 | 0 | > 300 | 4.3 | 0 | > 300 | 4.1 | 0 | 297 | 3.4 | 0 | 300** | 3.9 |

* Data for individual subjects is given because of the variability shown.

** Afterglow extinguished at 300 seconds.

zero in all cases and the char areas of 2.4 and 2.2 are comparable to the results obtained with control specimens. One laundering subsequent to the wear periods also exhibited no deleterious effects upon the flameproof properties.

In the course of similar tests of Type 3 garments, the subjects produced an average of 1200 grams of sweat in the 3-hour period and 2150 grams after 6 hours. These amounts of perspiration had no significant effect upon the flame resistance of this antimony oxide-vinyl resin treatment. The worn garments exhibited no afterflaming, even after laundering, with the exception of some specimens of one uniform. The afterglow was characteristically high in all cases but apparently was not enhanced by the perspiration. In most of the tests of the 6-hour garments the afterglow was quenched after 300 seconds. This accounts for the low char area in those specimens.

### c. Rainfall

As a further comparison of the relative merits of the three types of flameproofed uniforms being considered, tests were conducted to determine the effect of artificial rainfall upon the flameproofness and tensile strength of the treated garments. Fortunately, previous experiments had supplied sufficient information to assign exposures of appropriate duration and intensity to each of the three types of treatment. Correspondingly, the Type 1 uniforms, treated with the water-soluble mixture, were subjected to a mild exposure of 0.1 inch per hour for 50 minutes. This was just long enough to cause saturation of the garment. The durably treated Type 2 garments were exposed to a fall of 3 inches per hour for a period of 12 hours. Type 3 uniforms, possessing a permanent but non-glow-resistant treatment, were subjected to a rate of 3 inches per hour for a total of 3 hours. With the exception of these differences in the intensity of the rain, the garments were all tested under identical experimental conditions.

In order to keep the subjects sufficiently warm throughout the test period, they wore considerable clothing under the test garments. This dress consisted of 50–50 underwear, 2 pairs of wool ski socks, 1 pair of wool cushion-sole socks, M–1944 shoepacs, wet weather trousers and a wet weather parka. Dressed in this manner, six subjects in each type of test uniform entered the rain court and remained for the desired time. They were permitted to walk, run and play any games which did not involve undue abrasion or wear. At the end of the test period, the uniforms were sampled and tested according to the techniques previously described.

The results of these tests, the averages of which are presented in Table 19, indicate that the 50-minute exposure to a mild rain of 0.1 inch per hour was sufficient to destroy the efficacy of the 7:3:5 treatment used on Type 1 uniforms. The shoulders and knees, which were subjected to greater exposure and hence greater leaching were most seriously affected,

Table 19. Effect of Rainfall on the Flameproofed Uniforms, Types 1, 2 and 3

(*45°-Microburner Flame Test*)

| | | | Jacket | | | | | | | | | Trousers | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | |
| Uniform | Intensity in./hr. | Duration | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² |
| Type 1 | 0.1 | 50 min. | –[1] | – | – | 2 | 0 | 2.4 | 1 | 0 | 2.4 | 4 | 0 | 2.5 | –[2] | – | – | – | – | – |
| Type 2 | 3 | 12 hrs. | 0 | 0 | 2.8 | 0 | 0 | 2.6 | 0 | 0 | 2.6 | 0 | 0 | 2.7 | 0 | 0 | 2.8 | 0 | 0 | 2.7 |
| Type 3 | 3 | 3 hrs. | 0 | * | 2.4 | 0 | * | 2.3 | 0 | * | 2.3 | 0 | * | 2.3 | 0 | * | 2.1 | 0 | * | 2.3 |

* Afterglow in excess of 100 seconds.

[1] All specimens exhibited excessive afterflaming; 4 of 6 completely consumed by afterflame.

[2] All specimens exhibited excessive afterflaming; 2 of 6 completely consumed by afterflame.

the other portions of the garments retaining the majority of the original flameproof properties. It is apparent, nevertheless, that exposure to an amount of artificial rain barely sufficient to wet the fabric destroyed the flameproofness of the Type 1 uniforms.

The much more severe conditions employed with the two types of durably treated uniforms did not produce any noticeable changes in the flameproof characteristics. An exposure of 12 hours to a rainfall of 3 inches per hour did not alter the flame or glow resistance of the Type 2 uniforms. Similarly, flame test data on Type 3 uniforms, after being subjected to 3 hours of wear in a rain of 3 inches per hour, were comparable to that obtained with unused control garments.

### d. Sea Water

Because of the amphibious landings involved in military operations, considerable attention has been paid to the resistance of flameproofed fabrics to immersion in sea water. To supplement the laboratory experiments previously described, a series of practical tests were carried out wherein human subjects actually wore the treated uniforms into the ocean. Since the necessary facilities were not available at the Climatic Research Laboratory, a suitable site was selected at Washburn Island, 150 yards off the south shore of Cape Cod, with the cooperation of representatives from Headquarters, Camp Edwards, Massachusetts.

Six of each of the three types of treated uniforms were worn in sea water for a total of 30 minutes, according to the following progression:

| Immersion Period (min.) | Extent of Immersion |
|---|---|
| 25 | Up to knees |
| 3 | Up to waist |
| 2 | Up to neck |

Thus, these garments were subjected to a progressive immersion resembling an amphibious operation in reverse. During the immersion period the activity was controlled by having the subjects march under supervision. At the end of the test the uniforms were dried for 24 hours and returned to the laboratory where they were conditioned, sampled and tested according to the techniques described in Section a. After test specimens had been cut, the remnants of the uniforms were rinsed for 5 minutes with fresh water in a semi-mobile laundry washer, reconditioned for 24 hours and additional specimens cut and tested.

In the case of the Type 1 uniforms, practically all flame test specimens taken subsequent to the sea water immersion were completely consumed by flame. In no case did any specimen show significant retention of effective flame retardancy. For this reason the data on these garments are not presented here. Suffice it to say that even when certain sections were im-

Table 20. Effect of 30-Minute Progressive Immersion in Sea Water on Flameproofed Uniform, Type 2

*(45°-Microburner Flame Test)*

| | Jacket | | | | | | | | | Trousers | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | |
| | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | After-flame sec. | After-glow sec. | Char Area in² | Mean Afterflame sec. |
| Before Rinsing | 18 | 0 | 5.6 | 1 | 0 | 2.9 | 35 | 0 | B.E.* | 46 | 0 | B.E. | 38 | 0 | B.E. | 28 |
| | 34 | 0 | B.E. | 39 | 0 | B.E. | 0 | 0 | 2.6 | 34 | 0 | B.E. | 44 | 0 | B.E. | 30 |
| | 0 | 0 | 2.3 | 3 | 0 | 2.8 | 28 | 0 | B.E. | 43 | 0 | B.E. | 47 | 0 | B.E. | 24 |
| | 0 | 0 | 2.7 | 1 | 0 | 2.5 | 5 | 0 | 2.5 | 45 | 0 | B.E. | 46 | 0 | B.E. | 19 |
| | 0 | 0 | 3.1 | 43 | 0 | B.E. | 38 | 0 | B.E. | 40 | 0 | B.E. | 59 | 0 | B.E. | 36 |
| | 0 | 0 | 2.4 | 1 | 0 | 2.4 | 29 | 0 | B.E. | 34 | 0 | B.E. | 45 | 0 | B.E. | 22 |
| | 24 | 0 | B.E. | 49 | 0 | B.E. | 46 | 0 | B.E. | 50 | 0 | B.E. | 54 | 0 | B.E. | 45 |
| Mean | 11 | – | — | 20 | – | — | 26 | – | — | 42 | – | — | 48 | – | — | 29 |
| After Rinsing | 63 | 0 | B.E. | 57 | 0 | B.E. | 68 | 0 | B.E. | 50 | 0 | B.E. | 61 | 0 | B.E. | 60 |
| | 35 | 0 | B.E. | 38 | 0 | B.E. | 46 | 0 | B.E. | 37 | 0 | B.E. | 56 | 0 | B.E. | 42 |
| | 1 | 0 | 3.0 | 45 | 0 | B.E. | 51 | 0 | B.E. | 56 | 0 | B.E. | 61 | 0 | B.E. | 43 |
| | 37 | 0 | B.E. | 48 | 0 | B.E. | 47 | 0 | B.E. | 56 | 0 | B.E. | 59 | 0 | B.E. | 49 |
| | 40 | 0 | B.E. | 52 | 0 | B.E. | 50 | 0 | B.E. | 71 | 0 | B.E. | 64 | 0 | B.E. | 55 |
| | 1 | 0 | 2.6 | 47 | 0 | B.E. | 39 | 0 | B.E. | 51 | 0 | B.E. | 61 | 0 | B.E. | 40 |
| | 43 | 0 | B.E. | 46 | 0 | B.E. | 52 | 0 | B.E. | 58 | 0 | B.E. | 59 | 0 | B.E. | 52 |
| Mean | 31 | – | — | 48 | – | — | 50 | – | — | 54 | – | — | 60 | – | — | 49 |

* B.E.—Burned to the end; not completely consumed.

Table 21. Effect of 30-Minute Progressive Immersion in Sea Water on Flameproofed Uniform, Type 3

*(45°-Microburner Flame Test)*

| | Jacket | | | | | | | | | Trousers | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Shoulder | | | Lower Back | | | Front | | | Seat | | | Knee | | | Mean | | |
| | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ | After-flame sec. | After-glow sec. | Char Area in $^2$ |
| Before Rinsing | 0 | * | 2.6 | 0 | * | 2.4 | 0 | * | 2.3 | 0 | * | 2.5 | 0 | * | 2.3 | 0 | – | 2.4 |
| | 0 | * | 2.3 | 0 | * | 2.2 | 0 | * | 2.2 | 0 | * | 2.3 | 0 | * | 2.2 | 0 | – | 2.3 |
| | 0 | * | 2.6 | 0 | * | 2.5 | 0 | * | 2.4 | 0 | * | 2.1 | 0 | * | 2.1 | 0 | – | 2.3 |
| | 0 | * | 2.7 | 0 | * | 2.5 | 0 | * | 2.2 | 0 | * | 2.6 | 0 | * | 2.3 | 0 | – | 2.5 |
| | 0 | * | 2.4 | 0 | * | 2.5 | 0 | * | 2.2 | 0 | * | 2.2 | 0 | * | 1.7 | 0 | – | 2.2 |
| | 0 | * | 2.6 | 0 | * | 2.9 | 0 | * | 2.9 | 0 | * | 2.4 | 0 | * | 2.6 | 0 | – | 2.7 |
| Mean | 0 | – | 2.5 | 0 | – | 2.5 | 0 | – | 2.4 | 0 | – | 2.4 | 0 | – | 2.2 | 0 | – | 2.4 |
| After Rinsing | 0 | * | 2.4 | 0 | * | 2.8 | 0 | * | 2.4 | 0 | * | 2.1 | 0 | * | 2.2 | 0 | – | 2.4 |
| | 0 | * | 2.6 | 0 | * | 2.2 | 0 | * | 3.0 | 0 | * | 2.7 | 0 | * | 2.5 | 0 | – | 2.6 |
| | 0 | * | 3.5 | 0 | * | 2.7 | 0 | * | 3.3 | 0 | * | 3.2 | 0 | * | 2.9 | 0 | – | 3.1 |
| | 0 | * | 3.2 | 0 | * | 2.5 | 0 | * | 2.6 | 0 | * | 2.6 | 0 | * | 2.1 | 0 | – | 2.6 |
| | 0 | * | 3.3 | 0 | * | 3.3 | 0 | * | 3.1 | 0 | * | 2.7 | 0 | * | 2.9 | 0 | – | 3.1 |
| | 0 | * | 3.3 | 0 | * | 2.6 | 0 | * | 2.8 | 0 | * | 2.4 | 0 | * | 2.5 | 0 | – | 2.7 |
| Mean | 0 | – | 3.1 | 0 | – | 2.7 | 0 | – | 2.9 | 0 | – | 2.6 | 0 | – | 2.5 | 0 | – | 2.8 |

* Afterglow in excess of 100 seconds.

mersed for only 2 minutes the leaching removed sufficient amounts of the 7:3:5 mixture to destroy completely the flameproof properties of those sections of the uniforms.

The data of Table 20 indicate that the resistance of this particular urea-phosphate type treatment to sea water immersion was not much greater than that of the water-soluble mixture. After the sea water experiments the Type 2 uniforms showed excessive afterflaming. Specimens from the seat and knee were consumed by afterflame to the limit of the specimen holder. Even in the case of shoulder regions, which experienced immersions of only 2 minutes, several of the test specimens showed more than 24 seconds afterflaming. The flame retardancy was still more seriously impaired by the fresh water rinse. After rinsing practically all specimens burned to the edge of the test frame. The results as a whole would indicate that the flameproof properties of the Type 2 uniforms were destroyed by a 2- to 5-minute immersion in ocean water. This effect of sea water is more striking when compared with the earlier leaching and laundering data. It serves to substantiate again the importance of ionic exchange mechanisms with this type of treatment as pointed out in Chapter V.

The results obtained with the Type 3 uniforms are summarized in Table 21. The immersion in sea water has had no apparent effect upon the flameproof properties of these garments. The specimens exhibited no afterflaming in any case and the fresh water rinse did not alter these characteristics. The afterglow was, as usual, highly excessive but was not enhanced by the ocean water immersions.

### e. Storage

During the course of the practical wear tests at the Climatic Research Laboratory all unused test uniforms were stored under usual stockroom conditions. These conditions were a temperature of approximately 70° F. and relative humidity of 30 to 50%. After six months of storage, one of each of the three types of uniforms was selected, sampled and tested according to the techniques previously described. The average results for flameproofness and tensile strength are presented in Table 22.

Table 22. Effect of Six Months' Stockroom Storage on the Flameproofed Uniforms, Types 1, 2 and 3

*(45°-Microburner Flame Test; 1-inch Raveled Strip Tensile Test)*

| Uniform | When Tested | Afterflame sec. | Afterglow sec. | Char Area in² | Tensile Strength lbs./in. |
|---|---|---|---|---|---|
| Type 1 | Before storage | 0 | 0 | 2.4 | 99 |
| | After storage | 6 | 9 | 2.7 | 92 |
| Type 2 | Before storage | 0 | 0 | 2.4 | 106 |
| | After storage | 0 | 0 | 2.1 | 100 |
| Type 3 | Before storage | 0 | 624 | 5.2 | 120 |
| | After storage | 0 | 752 | 6.9 | 126 |

Although some failures in the Type 1 uniform can always be attributed to an uneven distribution of retardant, the high incidence of defective specimens in this series of tests indicated that 6 months' storage had a deleterious effect upon the flameproof properties of these treated garments. The mean values shown in Table 9 indicate that there has been a reduction in the resistance to both afterflame and afterglow. This is in agreement with the findings reported in Section B–1–a of this chapter and correlates well with the decomposition tendencies displayed under extreme storage conditions as summarized in Table 4. The loss of retardancy suffered has been attributed to the volatility of boric acid particularly in the presence of acid salts. Once again, it is apparent that with water-soluble mixtures of this type which contain boric acid or its weak base salts, periodic checks should be made in the course of storage to determine the extent to which retardancy is retained. The tensile strength of the Type 1 uniforms, under the conditions stated, was not significantly affected by 6 months' storage.

In contrast to the temporary treatment, Type 2 uniforms showed no noticeable loss of either flameproofness or fabric strength as a result of the storage period. The flame and tensile test data are essentially the same as that obtained with initial control specimens.

In the case of the Type 3 garments, the extensive afterglow which occurred makes it difficult to determine whether storage adversely affected the finish. The increase in char area over that of original control specimens is probably attributable to the longer afterglow. The difference, in any case, is not great considering the excessive original afterglow and it may be concluded that 6 months' storage did not appreciably impair the antimony oxide-vinyl resin type of treatment. Similarly, the tensile strength of Type 3 garments was not decreased in the course of this storage period.

### f. Accelerated Wear *

In addition to the preceding experiments carried out under more or less normal conditions of use and storage, a series of accelerated wear tests were performed on the durably treated garments. This work was carried out by the staff of the Quartermaster Board at Camp Lee, Virginia. The experimental studies were still in progress at the time that this report was compiled, and for this reason the findings reported in the following pages may be considered as preliminary conclusions based upon the data available. Final verification will depend upon a statistical analysis of the relative wearing qualities of the several treated fabrics as determined through a study of the comparative wear scores and analysis of the types and degree of failures at the completion of the test.

A description of the Quartermaster Board Combat Course on which

* Contributed by Robert W. Little.

these tests were performed has been given in Chapter IV, Section B–11. The objective of this type of test is to predict the serviceability of garments under the rigorous conditions of wear likely to be encountered in the course of combat operations. As will be shown shortly, these tests are valuable supplements to those carried out under normal conditions of usage, particularly in the case of the urea-phosphate type of treatment, where the fabric may be appreciably degraded in the course of the flameproofing treatment.

Two of the sets of uniforms involved in this series of Quartermaster Board tests are essentially the same as the Type 2 and Type 3 garments described on page 321. In addition, three fabrics were commercially processed with the urea:diammonium phosphate (UDAP) treatment as discussed on page 208. The purpose of these wear tests was to determine to what extent the life of these garments was reduced as a result of the loss in tensile strength resulting from the flameproofing treatment. The three fabrics selected also afford a measure of the effect of the base fabric and its condition prior to impregnation upon the wearing qualities of the resulting flameproofed garment. A comparison with the performances obtained in laboratory tests is also possible since the three treatments employed are essentially the same as those described for Q.M.C. #27 fabric #4, commercial product M–3, and C.W.S.–M.I.T. fabric on pages 309 and 310. In every case, the cloth was processed in the form of yard goods on a commercial scale and subsequently fabricated into fatigue uniforms. The treated garments tested at Camp Lee had been constructed with the fabric face out in one series and with the fabric back on the outside in the other. For the purposes of this discussion only the "face out" specimens have been considered.

In conducting the tests, all jackets were worn inside the trouser waist bands and the trouser cuffs were worn inside combat boots. After every second traversal of the course, the garments were laundered in a mobile laundry unit, using Mobile Laundry Formula I as specified for general handling of cotton fabrics (see page 323). Following laundering, the garments were charted in accordance with the Quartermaster Board Scoring System.

In this particular series of tests it was found to be neither practical nor advisable to assign a wear score to the garments. In many cases the flame-retardant treatment affected the wearing characteristics of the garments to such an extent that they no longer afforded protection to the wearer after one traversal of the Combat Course. This fact could not be definitely shown in a wear score analysis and therefore the data have been presented in a somewhat different fashion as shown in Table 23.

Based upon this criterion of the number of traversals of the Combat Course which the garment will withstand, it is readily apparent that the decrease in tensile strength produced by the urea-phosphate type of treat-

Table 23. Resistance of Durably Flameproofed Uniforms to Accelerated Wear Tests

*(All garments constructed with fabric face out)*

| | Grey H.B.T., Untreated | | Grey H.B.T., UDAP Treated | | Standard H.B.T., OD #7 UDAP Treated | | 9-oz. Sateen, UDAP Treated | | Type 2 Garments | | Type 3 Garments | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Jacket | Trousers | Jackets | Trousers | Jackets | Trousers | Jackets | Trousers | Jackets | Trousers | Jackets | Trousers |
| Warp Tensile Strength, lbs./in. (1″ strip) — Untreated | 140 | | 131 | | 132 | | 145 | | 131 | | 110 | |
| Warp Tensile Strength, lbs./in. (1″ strip) — Treated | — | | 65 | | 76 | | 65 | | 88 | | 104 | |
| Number of garments in test | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 16 | 16 |
| Number of garments remaining in test on June 17, 1946 | 4 | 2 | 2 | 0 | 3 | 0 | 4 | 0 | 5 | 1 | 13 | 5 |
| Number of garments withdrawn from test before June 17, 1946 | 4 | 6 | 6 | 8 | 5 | 8 | 4 | 8 | 3 | 7 | 3 | 11 |
| Maximum number of traversals of combat course of those garments withdrawn from test | 8 | 9 | 8 | 7 | 8 | 2 | 7 | 6 | 8 | 7 | 9 | 9 |
| Minimum number of traversals of combat course of those garments withdrawn from test | 7 | 6 | 4 | 1* | 3.5 | 1* | 6 | 1* | 6 | 2 | 7 | 5 |
| Average number of traversals of combat course of those garments withdrawn from test | 7.7 | 7.2 | 6.2 | 2.2 | 5.7 | 1* | 6.5 | 2.5 | 7 | 4.2 | 8 | 6.7 |
| Maximum number of traversals of combat course of any garment up to June 17, 1946 | 9 | 9 | 9 | 7 | 9 | 2 | 9 | 6 | 9 | 7 | 10 | 9 |

* Less than one traversal.

ment is reflected in the wearing qualities of the garment. Considering only the herringbone twill uniforms, it is interesting to note that the serviceability in terms of resistance to this accelerated wear bears a direct relation to the tensile strength of the treated fabric. Apparently, in these few cases, the tear strengths are nearly equal or do not profoundly affect the wearing qualities. It is still very possible, however, that with other treatments the tear strength might be the limiting factor with respect to serviceability.

A comparison of the grey H.B.T. and standard H.B.T., both of which were processed with a UDAP treatment, does not show any striking effect of the pretreatment of the base fabric. In the former case the grey cloth was carefully desized and then dyed prior to flameproofing. The standard H.B.T. OD #7 was selected from run-of-the-mill fabric on hand and processed per se without any desizing treatment. As has been shown previously in Chapters V–B–1 and VI–B–1, a highly absorbent base cloth tends to produce a more even impregnation with better permanence under leaching and laundering conditions. The results in Table 23 suggest that this homogeneity of treatment may also be reflected in the serviceability of the fabric, though many other variables must also be considered.

The 9-oz. sateen fabric was also processed without any previous desizing treatment and is therefore comparable to the standard H.B.T. Comparison of these two sets of garments indicates that the construction of the sateen fabric is such that it is more resistant to severe wear conditions. This is particularly evident in the case of the trousers. The difference in performance is slight, however, and does not appear when the sateen is compared to the garments prepared from grey H.B.T.

In all cases it is noticeable that the trousers are subjected to more strenuous wear than the jackets. In many instances, differences in the serviceability of two differently treated garments are much more apparent in the histories of the trousers than in the comparable data on the jackets.

On the basis of the data available thus far, the following general conclusions may be drawn, bearing in mind that the results should be supported by a statistical analysis of wear scores and garment failures:

1. The Type 3 garments, treated with an antimony oxide-vinyl resin solvent suspension treatment, are approximately equal to untreated control garments in their ability to withstand conditions of severe wear. They are, furthermore, far superior in this respect to any of the other flame-resistant uniforms tested in this group.

2. The Type 2 garments, processed by a commercial method of the urea-phosphate type, are definitely inferior to the control garments in their ability to withstand the rigors of combat wear but are better than the UDAP-treated uniforms.

3. The garments constructed of fabrics processed with the simple urea: diammonium phosphate treatment are unable to withstand severe wear

conditions and would undoubtedly prove to be unsuitable for combat use during extended operations.

It is well to point out at this time that these results should be interpreted carefully. As was shown in Chapter V, there is considerable latitude in the final fabric characteristics which may be attained by means of a urea-phosphate type of treatment. By varying the conditions under which the impregnated fabric is cured, almost any degree of esterification can be obtained along with varying degrees of cross-linkage and polymerization of the nitrogen-bearing salt grouping. If an extremely permanent treatment is desired and severe curing conditions are employed, the resulting fabric will be considerably degraded with respect to tensile strength. If, on the other hand, milder conditions are employed in the curing process the final fabric will have significantly higher strength with correspondingly less permanence. An example of the variations in fabric strength which may thus be produced can be seen in a comparison of the Type 2 garments considered in Tables 15, 17, and 23. Furthermore, by increasing the amount of material applied to the fabric it is possible to reduce the severity of the curing conditions and thus obtain permanently flameproofed fabrics possessing moderately high tensile strengths. For these reasons, the results presented in Table 23 must not be interpreted as a condemnation of the urea-phosphate type of treatment in general, but only of the particular conditions employed in this one case wherein the objective was a fabric of superior flameproofness and great permanence at low add-ons.

It is apparent that the urea-phosphate type treatments in general do suffer from a tendency to reduce fabric strength as a result of the flameproofing treatment. This must be overcome if a treated fabric is to be obtained which meets the requirements of efficient and permanent flameproofing at low add-ons and at the same time withstands the severe conditions of wear imposed by military usage. In evaluating the over-all desirability of any one flame-retardant fabric, however, it is necessary to consider the many other desirable characteristics as considered in the other sections of this chapter.

## 3. Physiological Evaluations

*William R. Christensen*

Although a uniform may possess satisfactory tensile strength and flameproof qualities, it cannot be accepted for general use if it imposes an excessive heat load upon the wearer, causes subjective discomfort, or produces other undesirable sequelae. Any of these conditions would encourage the wearer to discard the uniform and thereby lose the protection which it

affords. It is apparent, therefore, that selection of the flameproof uniform most desirable for combat wear requires physiological as well as physical evaluations.

A complete physiological evaluation would necessitate consideration of thermal insulation under cold conditions. For the purpose of this study, however, this is of minor importance and has been omitted in order to pursue a comprehensive investigation of imposed physiological heat load and subjective desirability. It should be apparent that under cold conditions heat load and such subjective criticisms as concern skin sensation, drag, etc., are of no importance. The flameproof uniform would be worn over heavy underclothing so that it could not affect the skin and a heavy heat load would not be detrimental. Since it is indicative of greater thermal insulation, those uniforms with greater heat loads would be superior for cold climate wear.

The data presented in this section were obtained from reports describing experiments conducted at the Armored Medical Research Laboratory, Fort Knox, Kentucky, and the Climatic Research Laboratory, Lawrence, Massachusetts. The techniques utilized differ slightly, but similar problems were investigated. The results collected by each laboratory will be discussed separately.

### a. Armored Medical Research Laboratory

Initial studies conducted at the Armored Medical Research Laboratory were reported in November, 1943.[4] They compare the heat loads imposed by one-piece, herringbone twill suits (coveralls) in their original unlaundered condition, after 2 to 6 months' wear with repeated laundering, and as flameproofed according to the suspension treatment developed at the Chemical Warfare Service Laboratories at the Massachusetts Institute of Technology. The flameproofing treatment consisted of impregnation with 22% antimony oxide and 12% Vinylite VYHH.

A total of thirty well-acclimatized soldiers were used as experimental subjects. They were participating, at the time of these studies, in long-term acclimatization experiments in which they remained continuously in a daytime environment of 90–91° F., relative humidity 92–95%, and night environment of 78–87° F., 60–85% relative humidity. In addition to the test garments they wore cotton shorts, cotton socks and either field shoes or jungle boots. All actual experiments were performed under conditions of the daytime environment. In the test routine, the soldiers acting as test subjects performed work of moderate severity, namely, walking at a standard pace while carrying a 20-pound pack. A walk of 2.5 miles in 47–50 minutes constituted a work period. A different uniform was worn during each period. The following observations were made:

[4] Armored Medical Research Laboratory 2(2–3, 18), pp. 1–6 (Nov. 24, 1943).

1. General appearance and subjective reactions were noted continuously and records kept of vigor, sweating, flushing, headache, and gastroenteric and cardiovascular disturbances.

2. Rectal temperature was taken with a clinical thermometer at the beginning and end of each work period.

3. At the beginning of each work period the resting pulse was taken in the erect position. At the end of each work period a count was made with the subject marking time.

4. The weight, within 10 grams, was obtained before and after each work period.

5. The clothes were weighed before and after some work periods.

The mean values of three of the measurements taken are as follows:

Table 24. **Physiological Reactions in Type 3 and Standard H.B.T. Uniforms**

| | Type 3 | Untreated H.B.T. New | Untreated H.B.T. Laundered |
|---|---|---|---|
| Heart Rate (per minute) | 138 | 140 | 128 |
| Rectal Temperature (°F.) | 100.8 | 100.1 | 100.2 |
| Weight Loss (grams) | 1375 | 1250 | 1100 |

From these data the Armored Medical Research Laboratory concluded that the Type 3 herringbone twill uniform imposed a slightly greater burden upon the wearer than did comparable untreated garments which had not been worn or laundered. The untreated garments which had been worn and laundered several times imposed the least burden. The authors also state that subjective sensations of discomfort agreed with the objective measures of physiological function.

Additional experiments comparing the heat loads imposed by the M.I.T.–C.W.S. antimony oxide treatment and the ordinary herringbone twill uniform were performed later.[5] In this study ten well-acclimatized soldiers acted as experimental subjects. The experimental technique was essentially the same as that described above except that the soldiers marched at the rate of 3 miles per hour and maintained this pace continuously for four hours except for short periods at the end of each hour at which time the experimental data were collected. The environmental conditions DB (Dry Bulb) 120° F., WB (Wet Bulb) 88° F., RH (Relative Humidity) 28%, were severe in relation to naturally occurring environments, but are known to occur frequently in industrial or military situations. The new herringbone twill garments and the Type 3 flameproof assembly were rotated among the experimental subjects according to the Latin Square method.

[5] Armored Medical Research Laboratory T–5, pp. 1–2 (July 31, 1945).

Table 25. Physiological Reactions in Type 3 and Standard H.B.T. Uniforms

| Uniform | Rectal Temperature Hours 1 | 2 | 3 | 4 | Pulse Rate/min. Hours 1 | 2 | 3 | 4 | Skin Temp. ° F. Hours 1 | 4 | Wt. Loss (Sweat) Gm./Hr. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H.B.T. | 100.7 | 101.6 | 101.9 | 102.2 | 131 | 121 | 118 | 123 | 98.9 | 99.7 | 1312 |
| Type 3 | 100.8 | 101.6 | 101.8 | 102.1 | 132 | 121 | 123 | 126 | 98.7 | 99.4 | 1426 |

On the basis of these data it was concluded that the Type 3 H.B.T. uniform had a heat load no greater than that of untreated uniforms. It is stated, however, that subjects objected to the antimony oxide flameproofed twill because it was too heavy.

The work of the Armored Medical Research Laboratory on flameproof clothing was supplemented later by the publication of data comparing the heat load imposed by new, untreated herringbone twill suits with that of similar garments flameproofed by means of a commercial urea-phosphate type treatment (Type 2).[6] The experiments were performed under two different environmental conditions, as follows:

1. D.B., 120° F.; W.B., 86° F.; R.H. 26%.
2. D.B., 88° F.; W.B., 84° F.; R.H. 85%.

The experiments were the same as those described previously except that the men spent 5 hours a day in the test chamber, and walked continuously for 4 hours at 2.9 miles per hour. The data obtained may be summarized as follows:

Table 26. Physiological Reactions in Type 2 and Standard H.B.T. Uniforms

| Uniform | Rectal Temperature Hours 1 | 2 | 3 | 4 | Pulse Rate/min. Hours 1 | 2 | 3 | 4 | Skin Temp. ° F. | Wt. Loss (Sweat) Gm./Hr. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1. *D.B., 120° F.; W.B., 86° F.; R.H. 26%* | | | | | | | |
| H.B.T. | 100.5 | 100.5 | 100.5 | 100.4 | 117 | 117 | 115 | 117 | 97.5 | 1645 |
| Type 2 | 100.4 | 100.4 | 100.4 | 100.3 | 117 | 120 | 117 | 118 | 97.2 | 1659 |
| | | | 2. *D.B., 88° F.; W.B., 84° F.; R.H. 65%* | | | | | | | |
| H.B.T. | 99.6 | 99.8 | 99.8 | 99.9 | 99 | 99 | 96 | 98 | 94.2 | 789 |
| Type 2 | 99.8 | 99.9 | 99.9 | 99.9 | 102 | 101 | 101 | 101 | 94.1 | 843 |

On the basis of these data it was concluded that herringbone twill suits made of cloth treated by the urea-phosphate process do not impose any greater load on acclimatized men than similar untreated suits. It was also found that eleven of the twelve subjects preferred wearing the flameproofed garments to wearing ordinary untreated herringbone twill uniforms. None of the men had any complaints concerning these suits.

## b. Climatic Research Laboratory

The Climatic Research Laboratory also performed experiments for the purpose of determining the comparative physiological heat load imposed

[6] Armored Medical Research Laboratory T-5, pp. 1–4 (Sept. 28, 1945).

by each of the three types of flameproof uniforms.[7] In these experiments, laundered herringbone twill suits were used as a control and, as such, were compared with each of the three flameproof uniforms.

**Test Procedures.** These studies were pursued in the Jungle Chamber. The "typical" jungle conditions selected for the study were: dry bulb of 90° F., and a relative humidity of 85%. These conditions approximate those found in Burma during July.

In this Jungle Chamber it was possible to obtain the selected conditions. The temperature of walls, ceiling, and floor were maintained at the existing ambient temperature by circulation of hot water through radiant panels. During the course of the experimental day, the dry bulb rarely varied more than ± 1° F. and the wet bulb seldom more than ± 0.75° F. The variation in humidity was less than ± 2%. The wind velocity was 1.5 miles per hour. These conditions are slightly more severe than the jungle conditions used by the Armored Medical Research Laboratory, but are considerably milder than the extreme conditions used by that Laboratory.

All subjects were acclimatized, having been subjected to 8 months of Jungle Chamber exposure prior to these tests. During this period each soldier spent at least 3 hours a day, 5 days a week in the chamber. Of the 3 hours, at least 1 hour was spent in exercise.

The same routine was used in all exposures. It may be briefly described as follows:

1. After entering the chamber each soldier spent the first hour at liberty. During this time, he wore the test uniform but was allowed to do as he wished provided his activity did not include exercise. Reading, writing, playing cards, etc., were permitted.

2. After the initial hour of adjustment, the subject was weighed to an accuracy of ± 5 grams, his rectal temperature determined with an accuracy of ± .05° F. by means of a clinical thermometer, and his pulse recorded by auscultation. Immediately thereafter, the exercise period started. Each soldier spent 60 minutes walking on the treadmill at the standard rate of 3.5 miles per hour. He was dressed in jungle boots, cushion-sole wool socks, cotton shorts, and the test uniform. No rests were allowed and no measurements of any sort were recorded during exercise. No water was given during this period.

3. As soon as the 1-hour march had been completed, each subject stepped off the treadmill, at which time his pulse and rectal temperatures were determined. Thereafter he was wiped free of all sweat and weighed.

4. The uniform was weighed before initiation of the exercise and again after the completion of the exercise to determine its sweat uptake.

5. After these physical and physiological measurements were completed, the soldier again spent 1 hour in the chamber. As before, he was

[7] Climatic Research Laboratory No. 155, pp. 12–19 (Dec. 14, 1945).

allowed to do as he pleased. During this period most of the subjects spent their time sleeping.

6. Finally, each was interviewed and his subjective reaction to the adequacy and performance of the garment tabulated.

The data thus collected provide an adequate indication of the heat load during the period of exercise. The initial pulse and rectal temperatures were only of value in indicating that the subject was in a fairly basal state. In appraising the severity of the exposure, only the rectal temperatures and pulse rates at the end of the exercise period were considered. The difference between the initial and final weight is the total weight loss and represents the sum of the insensible water and sweat losses. Since the former is constant and relatively small, the weight loss is considered to represent the sweat loss. It is the most sensitive indicator of heat load. In addition, the initial weights of the garments and their moisture uptakes are presented. The percentage of total sweat taken up by the garments may be calculated from these data.

The fact that only two subjects are able to walk simultaneously on the treadmill in the Jungle Chamber limited the number of uniforms which could be compared in a single experiment. Each of the two subjects walking wore a different uniform. On the second day of the experiment the two types of outfits were exchanged. With this technique, a more adequate control of the experimental conditions was achieved.

**Comparative Studies.** In the first study, the standard H.B.T. uniform was compared with Type 1 flameproof uniform (see page 321). Only the means of the results are presented here.

Table 27. Experiment I — Comparison of Standard H.B.T and Type 1 Uniforms

*A. Physiological Reactions*

| | Wt. Loss, gms. (sweat rate) | | Rectal Temperatures at End of Exercise, ° F. | | Pulse, First 30 Seconds After Exercise (per min.) | |
|---|---|---|---|---|---|---|
| | *H.B.T.* | *Type 1* | *H.B.T.* | *Type 1* | *H.B.T.* | *Type 1* |
| Mean | 987 | 943 | 101.0 | 100.8 | 144.4 | 144.2 |

*B. Weight Data*

| | Original Wt., gms. | | Final Wt., gms. | | Difference, gms. (Moisture Uptake) | |
|---|---|---|---|---|---|---|
| | *H.B.T.* | *Type 1* | *H.B.T.* | *Type 1* | *H.B.T.* | *Type 1* |
| Mean | 1441.8 | 1389.1 | 1837.7 | 1839.8 | 395.9 | 450.7 |

*C. Subjective Reactions*

| Cooler | | | Less Drag | | | More Desirable Skin Sensation | | | General Preference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *H.B.T.* | *Type 1* | *Same* | *H.B.T.* | *Type 1* | *Same* | *H.B.T.* | *Type 1* | *Same* | *H.B.T.* | *Type 1* | *Same* |
| 3 | — | 6 | 1 | — | 8 | 8 | — | 1 | 8 | — | 1 |

The physiological reactions show that the mean sweat rate, rectal temperature, and pulse rate are all greater when the H.B.T. is worn than

when Type 1 is worn. When analyzed statistically, however, the differences are not significant in any instance. On inspection of the weight data, it is apparent that the Type 1 uniform which has at least a 12% add-on of the 7:3:5 mixture carries a slightly lower mean weight than the ordinary H.B.T. Since both uniforms were made of standard H.B.T., an explanation is in order. At the time this test was initiated, standard H.B.T. uniforms were not available through regular supply channels. Rather than delay the test, it was decided to use the H.B.T. uniforms supplied for another test. These garments were essentially the same as the regular H.B.T. uniforms. The fabric was identical, but the uniforms differed in the following particulars: (1) those used were fashioned with shoulder loops, safety flaps on the pockets, and gussets in the sleeves, while the standard H.B.T. uniform had none of these features; (2) the flameproof uniforms were equipped with resin buttons and the standard H.B.T. with metal buttons. These variations were sufficient to account for the difference in weight. Nevertheless, the difference in weight does not suffice to invalidate the comparative study. Therefore, disregarding these factors, it is apparent that Type 1 uniform takes up a significantly greater amount of water than the standard twill. This is undoubtedly caused by the presence of the water-soluble salts which enable the fabric to take up sweat more readily and in a larger amount. The fact that the sweat rate when Type 1 was worn was slightly less than when the standard H.B.T. was worn makes this effect even more striking. The subjective reactions are noteworthy. The soldiers were in good agreement concerning the relative coolness and amount of drag imposed by these two outfits. A majority of the subjects rated them as similar. However, in regard to skin sensation and general preference, the reaction was quite different. In both of these categories all but one man selected the untreated H.B.T. as the superior item. The remaining soldier noticed no marked difference. With the exception of the rating for coolness, all subjective reactions are statistically significant.[8] When given an opportunity to express an opinion concerning Type 1, all subjects stated that it was stiff, prickly, and irritating to the skin until it became thoroughly saturated with sweat. When saturated, it felt slimy. In summary, it is concluded that the impregnation of H.B.T. with the 7:3:5 causes no increase in its physiological heat load, but that untreated H.B.T. is preferred for its more desirable skin sensation.

When the standard H.B.T. was compared with Type 2 flameproof uniform (see page 321) no significant difference in imposed physiological heat load or comfort was detected. The mean results appear in Table 28.

Examination of the physiological data shows that the mean rectal temperature and pulse rate at the end of the hour of exercise are less for Type 2 than for the standard H.B.T. outfit. However, the mean sweat rate for Type 2 is slightly higher. Statistical analysis shows no significant difference between the two uniforms in any of these three categories. The

[8] Wet-Cold Field Trials, Washington (1945), Vol. I, Test Bulletin No. 24, Table II.

Table 28. Experiment II — Comparison of Standard H.B.T. and Type 2 Uniforms

*A. Physiological Reactions*

| | Wt. Loss, gms. (sweat rate) | | Rectal Temperatures at End of Exercise, ° F. | | Pulse, First 30 Seconds After Exercise (per min.) | |
|---|---|---|---|---|---|---|
| | *H.B.T.* | *Type 2* | *H.B.T.* | *Type 2* | *H.B.T.* | *Type 2* |
| Mean | 911 | 916 | 100.6 | 100.4 | 132.2 | 128.0 |

*B. Weight Data*

| | Original Wt., gms. | | Final Wt., gms. | | Difference, gms. (Moisture Uptake) | |
|---|---|---|---|---|---|---|
| | *H.B.T.* | *Type 2* | *H.B.T.* | *Type 2* | *H.B.T.* | *Type 2* |
| Mean | 1487.1 | 1452.7 | 1806.7 | 1786.5 | 319.7 | 333.8 |

*C. Subjective Reactions*

| Cooler | | | Less Drag | | | More Desirable Skin Sensation | | | General Preference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *H.B.T.* | *Type 2* | *Same* | *H.B.T.* | *Type 2* | *Same* | *H.B.T.* | *Type 2* | *Same* | *H.B.T.* | *Type 2* | *Same* |
| 3 | — | 6 | 3 | 1 | 5 | 5 | 1 | 3 | 4 | 1 | 4 |

imposed physiological heat loads of the two uniforms are, therefore, similar. Moreover, the original weights, final weights, and moisture uptakes of these two uniforms are essentially the same and there is no significant difference between the two in these respects. It is obvious, therefore, that the urea-phosphate flameproofing treatment has had no detectable effect on the moisture-absorbing properties of the H.B.T. fabric. Furthermore, the subjective reactions are in good agreement with the observed physiological values. Subjectively, there is no decided difference in the coolness, drag, or skin sensation of these two uniforms. As far as general preference is concerned, four men selected the standard H.B.T.; one chose Type 2 and four regarded the two as essentially similar. None of these subjective ratings is statistically significant. In view of the above observations, it may be concluded that there is no objective or subjective difference in the physiological heat loads imposed by these two garments and that, as far as wear in hot climates is concerned, they are equally comfortable.

A distinct difference between two uniforms appeared when the standard H.B.T. was compared with Type 3 flameproof uniform. The mean results appear in Table 29.

The mean weight loss, rectal temperature, and pulse rate for Type 3 are greater than those for the standard H.B.T. Statistical analysis shows a significant difference in both rectal temperature and pulse rate. This is justification for concluding that the heat load of Type 3 is greater than that of the untreated H.B.T. A partial explanation of this result can be found in the weight data. Type 3 uniform was heavier than the H.B.T. both at the beginning and at the end of the experiment. It did not absorb as much water, however, as the H.B.T. even though the subjects wearing it perspired more. The impermeable and nonabsorbent fabric did not transmit the water to the clothing surface for evaporation, and its effectiveness, therefore, was substantially diminished. The soldiers participating as subjects were unequivocal in their subjective rating of the two

Table 29. Experiment III — Comparison of Standard H.B.T. and Type 3 Uniforms

*A. Physiological Reactions*

| | Wt. Loss, gms. (sweat rate) | | Rectal Temperatures at End of Exercise, ° F. | | Pulse, First 30 Seconds After Exercise (per min.) | |
|---|---|---|---|---|---|---|
| | *H.B.T.* | *Type 3* | *H.B.T.* | *Type 3* | *H.B.T.* | *Type 3* |
| Mean | 1011 | 1059 | 100.5 | 100.8 | 138.8 | 156.5 |

*B. Weight Data*

| | Original Wt., gms. | | Final Wt., gms. | | Difference, gms. (Moisture Uptake) | |
|---|---|---|---|---|---|---|
| | *H.B.T.* | *Type 3* | *H.B.T.* | *Type 3* | *H.B.T.* | *Type 3* |
| Mean | 1458.8 | 1686.7 | 1875.6 | 2074.1 | 416.8 | 387.4 |

*C. Subjective Reactions*

| Cooler | | | Less Drag | | | More Desirable Skin Sensation | | | General Preference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *H.B.T.* | *Type 3* | *Same* | *H.B.T.* | *Type 3* | *Same* | *H.B.T.* | *Type 3* | *Same* | *H.B.T.* | *Type 3* | *Same* |
| 7 | — | 1 | 6 | — | 2 | 7 | — | 1 | 8 | — | — |

outfits. Seven of the eight considered the untreated H.B.T. to be cooler; one judged the two uniforms to be similar. The reactions concerning the desirability of skin sensation were identical. Two of the group felt that the amount of drag was similar; six considered the H.B.T. to be superior in this respect. As far as general, over-all preference was concerned, all subjects, without exception, selected the standard H.B.T. This is statistically significant. From all of the above data, it is apparent that the standard H.B.T. imposes less physiological heat load than Type 3 and is also much more desirable from a subjective standpoint.

After each of the test uniforms had been compared with the standard H.B.T., two studies were conducted in which one test uniform was compared with another. In the first study, Type 1 flameproof uniform was compared with Type 2. The mean results follow:

Table 30. Experiment IV — Comparison of Type 1 and Type 2 Uniforms

*A. Physiological Reactions*

| | Wt. Loss, gms. (sweat rate) | | Rectal Temperatures at End of Exercise, ° F. | | Pulse, First 30 Seconds After Exercise (per min.) | |
|---|---|---|---|---|---|---|
| | *Type 1* | *Type 2* | *Type 1* | *Type 2* | *Type 1* | *Type 2* |
| Mean | 1020 | 973 | 100.8 | 100.6 | 140.4 | 140.4 |

*B. Weight Data*

| | Original Wt., gms. | | Final Wt., gms. | | Difference, gms. (Moisture Uptake) | |
|---|---|---|---|---|---|---|
| | *Type 1* | *Type 2* | *Type 1* | *Type 2* | *Type 1* | *Type 2* |
| Mean | 1411.5 | 1428.3 | 1893.3 | 1847.8 | 481.8 | 419.6 |

*C. Subjective Reactions*

| Cooler | | | Less Drag | | | More Desirable Skin Sensation | | | General Preference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Type 1* | *Type 2* | *Same* | *Type 1* | *Type 2* | *Same* | *Type 1* | *Type 2* | *Same* | *Type 1* | *Type 2* | *Same* |
| 3 | 1 | 5 | 1 | 2 | 6 | 4 | 3 | 2 | 4 | 3 | 2 |

According to the physiological data, the mean weight loss and mean rectal temperature are lower for Type 2 than for Type 1. Although the trend of the data is in favor of Type 2, no difference of statistical importance exists in any of these categories. Therefore, the physiological heat load imposed by these two uniforms may be said to be similar. The uniforms are of the same material. Their thickness should be the same, and according to the weight data, their initial weights are almost exactly the same despite the fact that they were flameproofed by two different methods. The moisture uptakes of the two uniforms are similar. Even though the weight gain of Type 1 is greater than that of Type 2, the fact that the mean sweat rate was greater in the former tends to compensate for this difference. It is apparent from the subjective reactions that the men who wore these uniforms did not prefer one to the other. There is no definite trend in favor of either in regard to coolness, drag, skin sensation, or over-all preference. As far as these studies are concerned, therefore, there is no objective or subjective preference for one or the other.

Quite different results were collected when Type 2 flameproof uniform was compared with Type 3:

Table 31. Experiment V — Comparison of Type 2 and Type 3 Uniforms

*A. Physiological Reactions*

| | Wt. Loss, gms. (sweat rate) | | Rectal Temperatures at End of Exercise, ° F. | | Pulse, First 30 Seconds After Exercise (per min.) | |
|---|---|---|---|---|---|---|
| | *Type 2* | *Type 3* | *Type 2* | *Type 3* | *Type 2* | *Type 3* |
| Mean | 898 | 972 | 100.8 | 101.1 | 139.8 | 149.8 |

*B. Weight Data*

| | Original Wt., gms. | | Final Wt., gms. | | Difference, gms. (Moisture Uptake) | |
|---|---|---|---|---|---|---|
| | *Type 2* | *Type 3* | *Type 2* | *Type 3* | *Type 2* | *Type 3* |
| Mean | 1437.4 | 1660.4 | 1792.1 | 2010.7 | 354.7 | 350.3 |

*C. Subjective Reactions*

| Cooler | | | Less Drag | | | More Desirable Skin Sensation | | | General Preference | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Type 2* | *Type 3* | *Same* | *Type 2* | *Type 3* | *Same* | *Type 2* | *Type 3* | *Same* | *Type 2* | *Type 3* | *Same* |
| 7 | — | 2 | 7 | — | 2 | 7 | — | 2 | 9 | — | — |

Inspection shows that the mean sweat rate, rectal temperature, and pulse rate are all higher when Type 3 is worn than when Type 2 is worn. Statistical studies show that there is a real difference in both the sweat rates and the pulse rates. This is ample justification for concluding that the physiological heat load imposed by Type 3 is greater than that imposed by Type 2. The weight data give some indication of the reason for this finding. Type 3 is heavier both initially and at the completion of the hour of exercise. However, despite the fact that the mean sweat rate was much greater in the Type 3 uniform, its mean moisture uptake is approximately the same as that of Type 2. This can be taken as a further indica-

tion of an important fact, namely, that Type 3 is a relatively water-repellent fabric. It wets through slowly so that evaporation takes place from its outside surface only after a relatively long period of time. The subjective reactions are in good general agreement with the objective physiological results. Of the nine soldiers participating, seven felt that Type 2 was the cooler of the two uniforms; two could detect no difference. Seven considered Type 2 to have less drag; two considered the two to be similar. Seven selected Type 2 as the most desirable in regard to skin sensation; the reactions of the remaining two were equivocal. The general over-all preference was unanimously in favor of Type 2, a finding which is statistically significant. All things considered, Type 2 is the cooler and subjectively more desirable uniform. The results of these studies may be summarized as follows:

The heat loads imposed by the standard H.B.T., Type 1 and Type 2 are similar and less than that of Type 3. Since Type 1 was not compared with Type 3, the conclusion that it is cooler than Type 3 is not completely justified. However, the fact that its heat load is the same as that of both the H.B.T. and Type 2, each of which is cooler than Type 3, is felt to warrant this presumption. The subjective results do not fall into line as precisely as these physiological data. Whereas the H.B.T. was selected in preference to Type 1 with only one exception (nine subjects) and opinion concerning H.B.T. and Type 2 was about equally divided, there was no definite subjective trend favoring Type 2 over Type 1 as would have been expected. It is quite obvious that, from a subjective standpoint, Type 3 is the least satisfactory for wear in hot areas.

Throughout the physiological heat load studies and in additional experiments wherein soldiers wore the flameproof uniforms,[9] special attention was devoted to the appraisal of the general reaction of the subjects. Stiffness and roughness of the fabric were obvious defects of some of the uniforms. In addition, there were the potential dangers that some of the flameproof chemicals might be toxic or that the wearers might become sensitive to them. Because of this, considerable time was spent in collecting subjective appraisals of the uniforms. Periodic examinations were performed to detect the presence of any skin or systemic disturbances. The salient observations concerning each of the three types of uniforms were as follows:[10]

**Type 1.** The method used in impregnating the Type 1 uniform resulted in the defect of uneven distribution of the crystalline flameproofing salts throughout the uniform fabric. In those spots where their concentration was especially high the fabric was very stiff; in other areas where the concentration was somewhat less there was still sufficient salt for formation of large crystals. Eleven subjects wearing this uniform com-

[9] See Section 2 of this chapter.

[10] Climatic Research Laboratory No. 155, pp. 44–45 (Dec. 14, 1945).

plained that it was stiff, uncomfortable and rubbed and caused irritation of the neck, axillae, and between the legs during the initial period of wear. Thereafter this defect slowly disappeared. In some instances, the soldiers spent considerable periods of time working the fabric manually so that the hand might be improved. Despite this marked subjective feeling against the uniform, there was no instance of any irritation requiring medication or attendance at sick call. The test exposures during which this uniform was worn involved continuous wear by a group of six men for a period of one week under laboratory conditions, and shorter exposures by larger groups of men under wet and hot ambient conditions. A large sampling of men, therefore, were subjected to the uniform under a variety of conditions assuring intimate contact with the body. The nature of the flameproofing salts, borax, boric acid and diammonium acid phosphate is such that no toxic effects would be expected unless large areas of the body were abraded so that heavy absorption could occur.

**Type 2.** The physical characteristics, *i.e.*, appearance, hand, and flexibility, of this uniform had been very little altered by the flameproofing treatment. There was no question that this was the most desirable of the three test items from the subjective standpoint. Its properties were essentially the same as those of the original H.B.T. Therefore, there were no complaints of stiffness, irritation or undesirable skin sensation. The most serious consideration concerning this garment was the possibility of the polyamine resins producing skin sensitization or systemic effects. Although a total of over forty soldiers wore this uniform at one time or another, none developed dermatitis or showed any untoward systematic effects. Since some of the uniforms were worn in rain and others under conditions producing excessive perspiration, intimate contact with any water-soluble constituents of the treatment was assured. In the course of other tests, some uniforms were continually worn by as many as five subjects for periods as long as 12 weeks. Other groups of six men wore the uniform for 3, 6, 8, 9 and 12 weeks respectively. The length and type of exposure were sufficient, therefore, to bring out any deleterious effects that might have been expected.

**Type 3.** The physical characteristics of the H.B.T. material used in the uniforms studied at the Climatic Research Laboratory had been definitely altered by the antimony oxide-vinylite treatment. In contrast to untreated H.B.T. fabric and despite the fact that it had been extensively treated after impregnation, it was still relatively hard, non-absorbent and inflexible. These features seriously affected the subjective desirability of the uniform. All soldiers considered it unsatisfactory for ordinary wear. There were many complaints concerning its stiffness, heat load, and roughness. While all these defects became progressively less noticeable with successive launderings and wear periods, the characteristics of the fabric never approached that of untreated H.B.T. A total of forty men wore this

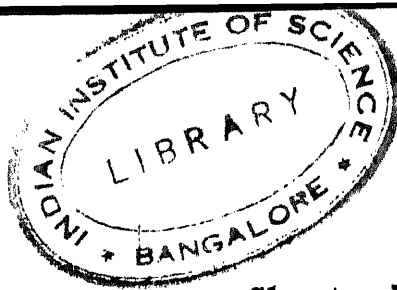
uniform for varying periods of time. In this case also the conditions of wear were extremely variable. The longest continuous exposure, by a group of six men, was for 6 weeks. Any deleterious water or sweat-soluble constituents of the treatment had ample opportunity to contact the skin because of exposures in Rain Chamber, Jungle Chamber, and sea water. Even under such difficult circumstances there was only one instance in which this uniform appeared to be responsible for causing a dispensary visit. A soldier, on the third day of wear under usual laboratory conditions, reported with a small boil on the inner surface of the right thigh. The roughness of the fabric had caused sufficient laceration of the skin for the development of a superficial infection. Other soldiers complained of minor irritation of the neck, axillae, and crotch but none attended sick call or required medication. From the Climatic Research Laboratory results, it may be concluded generally that no serious difficulties resulted from the wearing of any of the three types of uniforms but that only one of them, Type 2, could be considered highly satisfactory from a subjective standpoint when worn over the usual undershirt and shorts.

A comparison of the data of the Climatic Research Laboratory and the Armored Medical Research Laboratory shows that similar results were obtained with similar experiments on the same fabrics. Table 24, page 346, and Table 29, page 352, which give the results of comparison of untreated, laundered H.B.T. suits and the Type 3 flameproof garments performed at D.B., 90° F., R.H. 85% show that this type of flameproofing imposed an additional heat load. Table 26, page 347, and Table 28, page 351, reveal that at both laboratories no objective evidence was obtained which could be used to establish a preference for regular herringbone twill over the urea-phosphate treated herringbone twill. Subjects at both laboratories were in agreement that the regular herringbone twill suits were preferable to the antimony oxide-vinyl resin treatment. However, the urea-phosphate treated herringbone twill suits were preferred over the regular herringbone twill suits by the subjects at Armored Medical Research Laboratory and no significant preference was noted at the Climatic Research Laboratory.

When more severe conditions (D.B., 120° F.; W.B., 86° F.; R.H. 28%) were used at the Armored Medical Research Laboratory the objective findings lead to the same conclusion for the urea-phosphate type of treatment but not for the antimony oxide-vinyl resin treatment. For the latter treatment no objective evidence was obtained on which could be based a preference for either suit. Subjectively, however, the regular herringbone twill suit was preferred.

The exact reason for the discrepancy is not obvious. Several explanations can be suggested. First, it may be that with the severe environmental conditions under which the experiments were conducted, the subjects performed at such a high initial level that they did not respond significantly to heat loads which were only slightly different. In other words, both

objective conclusions may be valid for the experimental conditions used and the antimony oxide-vinyl resin treatment does impose noticeably greater heat load than regular herringbone twill at D.B., 90° F., R.H. 85%, but does not impose a noticeably greater heat load at D.B., 120° F.; W.B., 86° F.; R.H. 26%. Second, and closely related to the first explanation, it is apparent that the criteria for determining a significant difference varied from laboratory to laboratory. These physiological responses to heat have not yet been studied thoroughly enough to establish rigid criteria as to what constitutes a difference in heat load at various ambient conditions. Third, it is quite possible that the use of uniforms made of fabric from different production runs influenced the results. It has already been noted that, after impregnation with antimony oxide and vinyl resin, the fabric of the Type 3 uniform had to be subjected to extensive treatment before wearable garments could be made from it. Immediately after impregnation the material is extremely stiff, non-absorbent and virtually impermeable to air and water vapor. The subsequent treatment is intended to restore the original properties of the fabric. However, the success achieved in this respect varied markedly. Some mill runs were much more desirable than others. In this respect it is of great interest to compare the qualities of the fabric received by the two laboratories. Armored Medical Research gives the following description: "Antimony oxide-vinyl resin treated H.B.T. This garment had the appearance of untreated herringbone twill except that it had a smoother finish. It was not stiff or waxy. It wet as readily as the new H.B.T. Because of its increased ability to absorb water, these garments in use were heavier than the H.B.T." [11] In sharp contrast to this are the following quotations from the report of the Climatic Research Laboratory:[12] "The physical characteristics of the H.B.T. material used in this uniform were markedly altered by the antimony oxide-vinyl resin treatment. Even after the extensive mechanical softening, it was still relatively hard, non-absorbent, and inflexible. These features seriously affected the subjective desirability of the uniform. All soldiers considered it unsatisfactory for ordinary wear. There were many complaints concerning its stiffness, heat load, and roughness. While all these defects became progressively less noticeable with successive launderings and wear periods, the characteristics of this fabric never approached those of untreated H.B.T." There can be little doubt but that there was a decided difference between the uniforms tested at the two laboratories. Therefore, of the three explanations offered, the third is the most plausible. However, it is possible that all three contributed to the discrepancy. Under any circumstances both agree that the antimony oxide-vinyl resin treated garments are subjectively less desirable than regular herringbone twill.

[11] Armored Medical Research Laboratory T-5, p. 2 (July 31, 1945).
[12] Climatic Research Laboratory No. 155, pp. 44-45 (Dec. 14, 1945).

# Chapter VII

# Applications to Military Equipage

In addition to the studies of flameproofed Army clothing, there were many other instances in which retardant fabrics were developed for military purposes. Certainly, from a practical standpoint, the use of flameproofing treatments in the tentage program far exceeded that with respect to service uniforms from the standpoints of volume of production and operational service. It was felt to be desirable, therefore, to present the combined experiences of the Armed Services in the application of flame-resistant finishes to other military fabrics. It may well be that there were other similar, worthwhile programs which unfortunately were not known at the time that this volume was prepared.

## A. TENTAGE FABRICS

### 1. General Requirements

*Richard D. Wells*

Under the term "tentage" are classed the materials used in tents, paulins, awnings, hatch covers; and truck, weapon and implement covers. Tentage is primarily a protective material, providing shelter to materiel or personnel less well adapted to withstand environmental influences. It functions as a barrier against rain, wind, and sunlight, and in some military items against artificial light to satisfy black-out requirements. The selection of textile products to perform these functions, in preference to other barrier materials, is based on lightness of weight, ease of erection and removal, and compactness of the item when stored or shipped. The normal tentage material represents a working compromise between these desired properties as a barrier, the strength requirements for the item, acceptable degree of weight and flexibility, and cost or availability.

It is difficult to establish with any degree of finality a minimum rain resistance requirement by a laboratory method. In fact, a standard natural condition would first have to be defined in complex terms of rates, velocities, angles, and the contributing factors of wind and motion. Short of any such precise correlation, there is the general experience that certain fabric-finish combinations which have proved adequate barriers in use have showed performance above certain levels in the conventional laboratory

evaluation tests. For instance a minimum of 35 cm. in the hydrostatic head test,[1] or maximum of 10 cc. leakage under an 8-inch head for 10 minutes in the hydrostatic leakage test[2] have been generally recognized for material to be used in tents. Development of more realistic laboratory evaluations is progressing, though in attaining the velocity of natural rainfall the apparatus outgrows the usual laboratory facilities.

Wind resistance of tentage has not been of great concern as it is an automatic corollary to water resistance. In contrast to other functional requirements it comes to attention only when over-done, as air-impermeable barriers are not desired for most tentage because of moisture condensation on inner surfaces. Opaqueness to light is generally accomplished by the pigmentation required in attaining the desired color, which is usually of a dark shade.

Weight, strength, and flexibility requirements are relative to the size, design, and intended use of the end item. Within practical limits, minimum weight and maximum flexibility are sought. In some instances selection of a fire-retardant treatment may be based largely on the acceptable limit of weight for the finished item. The greatest quantity of tentage fabric procured by the Army in recent years has been duck and twill fabrics weighing from 11.5 to 12.5 ounces per square yard in the grey. With the normal 50% add-on of the fire-water-weather and mildew resistant finish, the total weight was approximately 18 ounces per square yard which was not considered excessive for the large tents not intended for carrying by pack. The only fire-resistant tentage for man-pack was of a 9-ounce material weighing less than 11 ounces per square yard when finished. Paulin materials weighed up to 30 ounces per square yard. In the conventional tent constructions, breaking strength in excess of 150 pounds per inch in the warp direction and 100 pounds per inch in the filling direction are considered essential. Flexibility, while originally judged by comparison to a standard sample, is now measured by the Tinius-Olsen instrument having a 0.5 inch-pound capacity. A maximum reading of 50 at a 20° deflection is allowed. It is important in tentage fabrics that flexibility is maintained at both high and low temperatures.

In the practical sense, the durability of the tentage material is equally as important as the initial properties. The continuity of its protective function is doubly significant in the economics of replacement rates, and loss or damage to the stores or equipment supposedly protected. In military usage considerations of economy may be in a much higher realm of values than the usual dollar unit. Durability may be considered in its two aspects as first the preservation of the fabric as a structural entity of sufficient

[1] Hydrostatic pressure test (low pressure range)—Section IV—part 5-c-(1), Federal Specification CCC-T-191a Supplement.

[2] Water permeability test—Section IV—part 5-c-(2), Federal Specification CCC-T-191a Supplement.

strength to withstand mechanical loads, and secondly the continuity of the functional properties. In the preservative category are the features of weather resistance, rot resistance and fire resistance, with the latter having additional value in minimizing danger of the tentage itself becoming a source of ignition for contained or adjacent property. These features are derived in part by selection of materials having natural resistance to the destructive agents, but more commonly by inclusion of additional components which offset inherent weaknesses of the base material. Continuity of function lies in the adhesion, insolubility, and chemical stability of both the finishing components required to perform the primary functions and those required for preservation. In attaining the total requirements a complexity of contributory substances may be required, with resulting problems of compatability and inter-action. Formulations will vary according to the relative importance of the various properties in the end use of the item. Degree of durability of the finish may also be based on the expected life of the base fabric under the mechanical abuse to be encountered by the end item. At the present stage of development, fire-resistant tentage should be expected to withstand one and a half to two years' continuous service depending on the severity of the climate, maintaining strength and functional properties to a useful degree during this period. The limiting factor is generally the loss in mechanical strength due to chemical and photo-chemical influences. While fire resistance will have been impaired to considerable extent in this time, modern mildew resistant treatments will still be found effective.

It can be seen from the preceding discussion that in tentage the attainment of fire resistance can be considered only in conjunction with many other factors. Many fire-resistant treatments are automatically excluded from consideration for lack of permanence under the severe conditions of weather. There are also some conflicts between the means for attaining the various features, as for instance the added flammability resulting from the use of one of the more efficient rot-proofers, copper naphthenate. Lacking a completely indestructible base material, the finishes for tentage must necessarily represent a compromise of desired properties.

## 2. Relative Suitability of Treatments

### a. Laboratory Evaluations

*Rogers B. Finch and Allan J. McQuade*

#### *(1) General Performance of Finish First Obtained Under Specification CCC–D–746*

Purchase of fire-resistant or flameproofed duck was initiated in August, 1941, and the first production followed within the next thirty days. The

performance of this material was to be governed by the requirements of Federal Specification CCC–D–746 entitled "Duck: Cotton, Fire, Water, and Weather Resistant."

The advantages claimed for the fire- and weather-resistant finish prior to its large procurement by the Quartermaster Corps were fourfold:

1. It gave a simple method of obtaining the new dark shade of olive drab recently adopted for tentage.
2. The finish was much more durable and would give water repellency over longer periods of time than other types of water-repellent and weatherproof finishes.
3. It was fire resistant.
4. It greatly increased the useful life of articles made therefrom which were exposed to weathering conditions such as light, mildew, heat, and water.

Knowledge of the materials used in effecting such a treatment had not been widely disseminated among the members of the textile finishing industry by those familiar with its development. Since Specification CCC–D–746 was of the performance type with no limitation as to the materials to be used and it was not required that the formula be registered with the bids, the exact composition of the compound used under that specification cannot be stated. However, based on information received from the various producers, an average composition for the fire-resistant finish for tentage in late 1941 would be as follows:

| | Per Cent by Weight |
|---|---|
| Chlorinated Paraffin | 19 to 23 |
| Chlorinated Rubber | 7 to 9 |
| Metallic Salt (Zinc Borate and Antimony Oxide) | 4 to 6 |
| Pigment | 8 to 12 |
| Filler | 4 to 6 |
| Solvent | 45 to 55 |

From the above it will be readily seen that the flameproofing process for the treatment of tentage duck depended on the combination of a metallic oxide and a chlorinated body, the mechanics for which have been previously discussed. In this instance the chlorinated paraffin and the chlorinated rubber provided the source of chlorine, while antimony oxide and other metallic salts completed the process. Where zinc salts were used, it was the opinion of some that these salts would provide adequate protection against mildew. This was later disproved. In this type of formulation, the chlorinated rubber also served as a binder or film former. The pigments for color purposes included synthetic or natural iron oxides, lead chromate, and shading colors such as carbon black and blue pigments. Those materials used as fillers included carbonates, employed as acid acceptors, and mica or aluminum stearate to obtain better resistance to water leakage.

The performance of this type finish appeared very satisfactory when fabrics were compared with requirements of the federal specification. However, the tentage fabric produced was subject to several complaints including serious deficiencies in mildew resistance and flexibility at low temperature. From the standpoint of handling at room temperature, drying to touch, and ability to resist passage of water, it was a very satisfactory finish.

### (2) *Effect Upon Performance of Major Changes in Formulation*

#### (a) *Replacement of Chlorinated Rubber With Other Binding Agents Under Specification CCC–D–746*

The first general change in the composition of the fire-resistant finish offered under Specification CCC–D–746 occurred about April, 1942. It became necessary to replace chlorinated rubber with various other binding agents since rubber was required for more important military usages. Some of the binding agents selected for this purpose were ethyl cellulose, vinyls, cumars, and rosin-modified phenol formaldehyde resins. In the case of the first three materials, plasticizers were incorporated with the resins to effect an improvement in flexibility at low temperature. Better grades of pigment were employed to eliminate ochres of high silica content and thus reduce wear of sewing machine parts.

These changes reflected themselves in improvement of some quality indices. In the case of fabric finished with a compound which included a vinyl, excellent hand and resistance to crocking resulted, though there were indications that afterflame time had been increased. It is not known whether this was influenced by the plasticized vinyl resin or by insufficient removal of the aromatic solvents required by its use.

The use of plasticized ethyl cellulose and cumar both resulted in improved flexibility of the finished fabric at low temperatures. Other considerations, notably poor tensile strength retention after outdoor exposure, resulted in the discontinuance of the use of the cumar resin. The causative factors of this failure were not investigated intensively, hence this action should not be considered as condemning the use of cumar.

The use of compounds which incorporated the rosin-modified phenol formaldehyde resins was reflected in poor flexibility of the finished product until a sufficient amount of plasticizer was employed.

Other changes of note were effected during this period. These included more general usage of 42% chlorinated paraffin to obtain improved flexibility at low temperature. In addition several pigment modifications took place in the effort to reduce wear upon sewing machine needles.

### (b) *Modifications of Compound with the Issuance of Tentative Specification J.Q.D. 242*

With the issuance of Tentative Specification J.Q.D. 242 in December, 1942, further changes in the flame-resistant finish were necessary as the result of the addition of new requirements over CCC–D–746. It has been pointed out that the latter was purely a performance type with little restriction on quality or type of materials used. J.Q.D. 242, however, included requirements in both these respects. Its requirements as to the incorporation of a mildew inhibitor, calcium carbonate, and chlorinated paraffin produced minor changes. In addition, the performance requirements were tightened up considerably with a relaxation only with respect to those concerning resistance to water leakage. Thus we now find the composition of the compound approaching the formula outlined below:

| | Per Cent by Weight |
|---|---|
| Chlorinated Paraffin | 13 to 17 |
| Binder | 7 to 9 |
| Antimony Oxide | 7 to 9 |
| Calcium Carbonate | 4 to 6 |
| Pigment | 9 to 12 |
| Mica or Aluminum Stearate | 1 to 2 |
| Pentachlorphenol | 1 to 2 |
| Solvent | 45 to 55 |

The above finish, as indicated by the accelerated weathering tests of the new specification, showed promise of greater durability. The addition of pentachlorphenol resulted in the material withstanding a 14-day soil burial period. If the fabric was leached for a 24-hour period prior to being subjected to burial, some instances of inferior performance resulted. Since the meaning of such performance was not known with respect to outdoor exposure and since there were considerable variations in the test results, it was felt that pentachlorphenol could be adopted, inasmuch as copper naphthenate was not, at that time, available for this program. Laboratory tests showed the crocking resistance of the above finish was somewhat inferior to that obtained with the original chlorinated rubber type. It also may be said that the latter was not always equal with respect to resistance to water leakage.

### (c) *Replacement of Pentachlorphenol by Copper Naphthenate Under Tentative Specification J.Q.D. 242*

In July, 1943, copper naphthenate was more available and a comprehensive series of exterior exposure tests had demonstrated the rapid loss of pentachlorphenol under such conditions. The use of copper naphthenate was then adopted. Because it was necessary to use larger quantities of

copper naphthenate as compared with pentachlorphenol and since it detracted from the fire-resistance qualities of the compound, it was necessary to increase the quantity of available chlorine in the compound. This in turn, under the requirements of J.Q.D. 242, often necessitated that the calcium carbonate content be increased. These increases had to be met by subtractions and hence we find that reductions in resin content and antimony oxide had to be effected. A composite formula would now approximate the following:

| | Per Cent by Weight |
|---|---|
| Chlorinated Paraffin | 18 to 22 |
| Binder | 2 to 4 |
| Antimony Oxide | 5 to 7 |
| Calcium Carbonate | 6 to 8 |
| Pigment | 7 to 9 |
| Mica or Aluminum Stearate | 2 to 3 |
| Copper Naphthenate | 4 to 6 |
| Solvent | 45 to 55 |

Though development samples had indicated satisfactory performance, duck finished on a production basis, showed a considerable decrease in fire resistance since the time of afterflame and the length of char increased and was evidenced by the treated fabric both before and after leaching. This condition was modified in early 1944 by the introduction of 70% chlorinated paraffin. The mildew resistance was considerably improved and no loss in this quality resulted from prolonged exposure. Some decrease in resistance to crocking was obtained due to the reduction in binder and the increase in the quantity of chlorinated paraffin.

(d) *Modifications Under Tentative Specification J.Q.D. 242 Produced During Critical Procurement Period from September, 1944, to August, 1945*

When large-scale procurements were initiated in the late summer of 1944, it was found that the supply of naphthenic acid for the manufacture of copper naphthenate had become insufficient because of increase in other important military uses; hence, the mildew inhibitor was modified to the extent that one-half the required copper content might be obtained from copper hydroxy naphthenate or basic copper oleate. Since these two materials possessed higher copper contents than did the type of copper naphthenate previously used, it was found that the amount of binder could be increased and thus approach its former quantity.

In the course of this large-scale production period it was necessary to allow the use of other grades of chlorinated paraffins and to restrict those finishers using a relatively high amount of antimony oxide to a maximum of 12% on the basis of the solid compound.

In tests of production material the use of 70% chlorinated paraffin was reflected in reduced afterflame and char length. On the other hand, soil burial tests indicated that the copper naphthenate extenders markedly decreased the mildew resistance. This was particularly emphasized in the case of substitute tentage fabrics requiring desizing prior to coating application.

### (e) *Modifications of Compound with Issuance of U.S.A. Specification 6–345*

Specification 6–345 was issued in July, 1945, when the demand for finished fabric had diminished to a point where restrictions upon the quantity of the critical raw materials employed could be removed. Since the requirements for fire resistance were made somewhat more severe, the principal result in the formulation of several compounds was to increase the use of the 70% type of chlorinated paraffin. In addition, normal copper naphthenate replaced the substitute combinations used during the period of high production. Thus the average formulation approximated the following:

| | Per Cent by Weight |
|---|---|
| Chlorinated Paraffin (42%) | 10 to 12 |
| Chlorinated Paraffin (70%) | 5 to 7 |
| Binder | 4 to 6 |
| Antimony Oxide | 5 to 7 |
| Pigment | 9 to 11 |
| Calcium Carbonate | 5 to 7 |
| Copper Naphthenate | 5 to 6 |
| Solvent | 45 to 55 |

Before there was opportunity using a revised sampling plan to determine whether these formula changes were reflected in higher quality levels, all finishing activities were terminated.

## *(3) Variations Produced by Different Methods of Formulating, Compounding, and Finishing as Indicated by Quality Control Chart Analysis*

In the foregoing paragraphs the authors have attempted to show the variations produced by different methods of formulating, compounding, and finishing of the entire industry as indicated by quality control chart analysis. It will be noted that variations in quality occurred in all stages of the finish development mentioned but those described are only those which are related to changes in formulation to effect specific improvements or to curtail the use of materials in excessive demand.

Methods of formulating and compounding differed considerably from

contractor to contractor. For instance, examination of the records shows, as indicated in the foregoing formulae, that the average antimony oxide content was 6%. Further investigation disclosed that between individual finishers the amount of this material incorporated varied from 3% to 12%. Despite such variations, there was a general uniformity in the level of performance of the finishers using such extreme antimony oxide contents and they did not show a significant departure from the level of performance for the entire industry.

In addition, variations were noted in the performance level of finishers using compound from the same source. One example noted in late 1944 concerned three finishers. It was the practice of one, Finisher A, to apply the compound using a relatively high ratio of solids to solvent and to follow with a short dry period at high temperature. Finisher B applied the compound in the same manner but passed his material over a stack of more than 50 dry cans using a lower temperature but his dry period was for a normal length of time. The third and last finisher, C, cut the compound with the solvent to provide a 1:1 ratio of solid to solvent. In addition, he removed the solvent by tunnel drying for a short period plus festoon drying for at least eight hours at a high temperature. As a result, the finished tentage duck from each concern showed a marked difference with respect to retention of char resistance after accelerated weathering as demonstrated by the following table:

Table 1. Per Cent Failure to Meet Requirements for Char Resistance After Accelerated Weathering Test of Tentative Specification J.Q.D. 242

| | Per Cent Failure (30 samples) |
|---|---|
| Finisher A | 63 |
| Finisher B | 23 |
| Finisher C | 93 |

A second instance of this type variation which occurred among a group of finishers using similar compound was noted in the flexibility of their finished duck. Some plants produced material which caused no difficulty in the plants of tentage manufacturers, while others were the source of frequent complaints. Upon investigation it was learned that those employing a shorter drying period with a high temperature were producing a fabric with better flexibility than those using a 20 degree lower temperature but with a 100% longer drying time.

When the product of an individual finisher is examined for any one quality with the use of control charts, considerable variation is noted. This should be expected since the method of sampling employed under J.Q.D. 242 as well as the test methods are sources of variation in themselves. These two coupled with the variations produced by methods used for constructing control charts and those outlined previously all lead to a large variation for any one quality of the finished product.

Illustrative of the variations resulting from the above, there are shown below four frequency distribution charts. The first, Figure 1, demonstrates the warp breaking strength of the finished fabric as a per cent change from

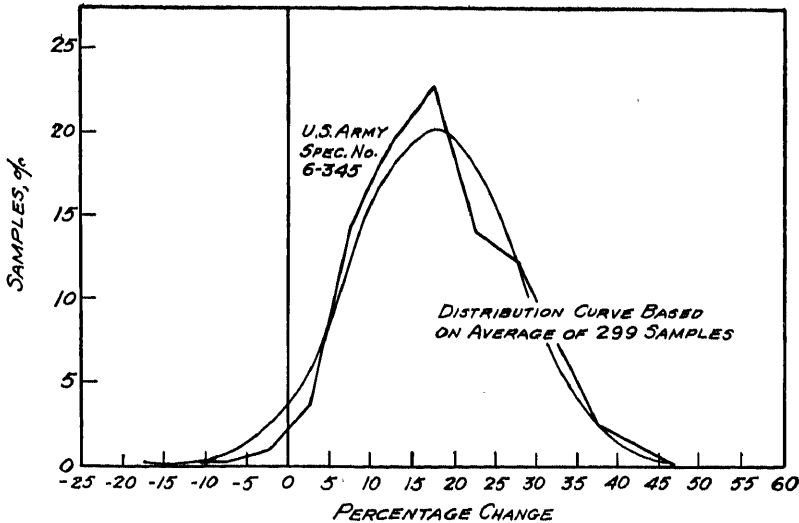



Figure 1. Frequency distribution curve for warp breaking strength as a per cent change from the original grey duck.

the original grey break. The wide spread in results emanating from variation in strength of grey duck plus variation influenced by the application of compound to the fabric produced the observed distribution of data.

In Figure 2 the initial warp breaking strength of finished fabric is plot-

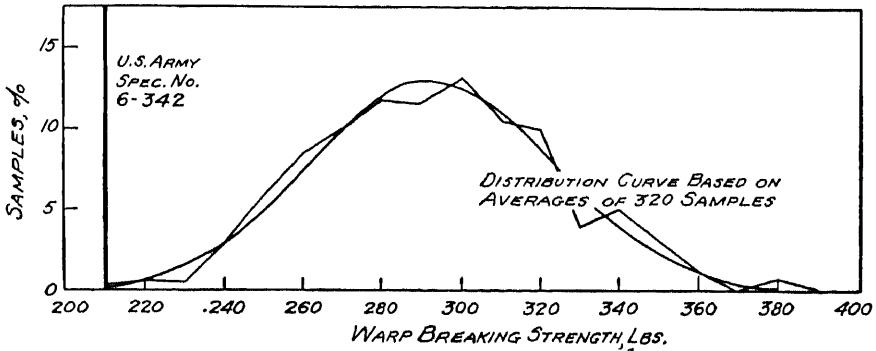



Figure 2. Frequency distribution curve for initial warp breaking strength in pounds.

ted and shows the variation entering into the calculations for Figure 1.

In Figure 3 the per cent change in warp breaking strength after accelerated weathering is plotted. Upon comparison with Figure 1, it will be noted that the introduction of an additional test procedure has effected

little or no change upon the shape of the curve and has served to slightly displace the mean on the abscissa in a negative direction.

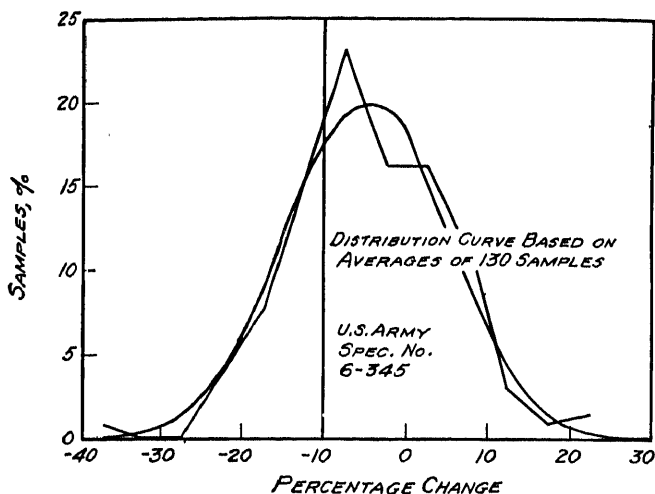



Figure 3. Frequency distribution curve for per cent change in warp breaking strength after accelerated weathering. (200 hours in National Çarbon Co. Unit X–1A operated with filter panels.)

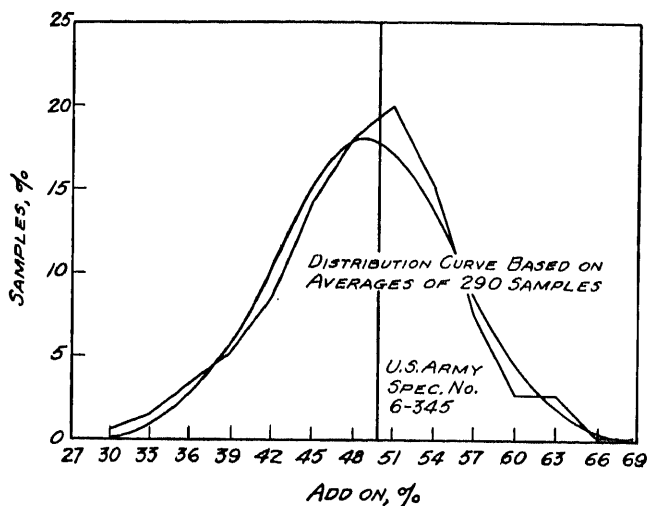



Figure 4. Frequency distribution curve for finished weight as the per cent increase over the grey weight.

In Figure 4 there are shown variations in the finished weight as the per cent increase over the weight of the grey duck. These are encountered due to the variations in the weight of the grey fabric as determined by standard laboratory methods, and the weight of the finish applied.

Under Tentative Specification J.Q.D. 242 attempts were made to control the raw materials entering into the finishing compounds in order to produce a product whose field performance would be uniform. Later, attempts were also made through the Quartermaster Corps Inspection Service to provide for a uniform sampling and testing plan. U. S. A. Specification 6–345 combines the best features of both into a plan capable of good quality control analysis. The termination of contracts in August, 1945, made it impossible to place this plan into full operation. It has not been possible, therefore, to judge the merits or demerits of such a quality control program from the standpoint of the adequacy of production control or to determine from such records the method of establishing specification performance levels and permissible tolerances.

### b. Performance Evaluations

*Henry A. Rutherford*

During March, 1943, seven samples of duck, cotton; fire, water, weather, and mildew resistant were procured by the Jeffersonville Quartermaster Depot for the purpose of evaluating the durability of the major group of compound types of early 1943 production. Although all of these samples were not necessarily representative of the average commercial production of each of these compound types, all of the finishers involved were working on contracts under Tentative Specification J.Q.D. 242. The major emphasis in the evaluation of these fire-resistant fabrics was placed on the observation of the retention of strength when they were exposed outdoors up to periods of 12 months at Washington, D. C.; Miami, Florida; New Orleans, La.; and Camp Young, Indio, Calif. In addition, all other performance requirements of the existing specifications were investigated, including a number of laboratory tendering tests. Because of the general interest of the weathering properties of the chlorinated paraffin-antimony oxide type of fire-resistant fabric, a fairly complete picture of their weathering characteristics is presented.[3]

The changes in breaking strength of this group of fabrics during exposure in the several locations up to one year are shown in Table 2.[4] It is readily noted that the fabrics vary considerably in resistance to outdoor weathering, but during the exposure in Washington, New Orleans and Miami all exhibited smaller losses in strength than the unfinished fabric. Thus, on the basis of these exposures, none of the finishes can be said to have accelerated the deterioration of the duck. During exposure in Indio, Calif., where hotter and less humid weather conditions prevailed, the ac-

[3] These data are compiled from reports on file at the office of the Quartermaster General, Washington, D. C.

[4] The exposures were made on panels set on racks at 45° facing toward the south.

Table 2. Changes in Breaking Strength of Duck, Cotton; Fire, Water, Weather, and Mildew Resistant, During Outdoor Exposure for Different Periods of Time at New Orleans (N.O.), La.; Miami (M.), Fla.; Washington (W.), D.C. (all beginning in April, 1943); and Camp Young, Indio (I.), Calif. (beginning July, 1943)

| Fabric | | Two Months | | | | Four Months | | | | Six Months | | | | Twelve Months | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | N.O. % | M. % | W. % | I. % | N.O. % | M. % | W. % | I. % | N.O. % | M. % | W. % | I. % | N.O. % | M. % | W. % | I. % |
| Un-coated | Warp | − 9 | − 4 | − 17 | − 17 | − 45 | − 21 | − 45 | − 25 | − 68 | − 58 | − 55 | − 28 | − 77 | − 45 | − 62 | − 42 |
| | Fill | − 19 | − 15 | − 25 | − 17 | − 55 | − 40 | − 40 | − 29 | − 68 | − 43 | − 49 | − 25 | − 77 | − 70 | − 62 | − 42 |
| A | Warp | + 3 | + 5 | + 4 | − 28 | − 17 | + 4 | − 8 | − 37 | − 40 | − 20 | − 15 | − 48 | − 77 | − 52 | − 20 | − 85 |
| | Fill | − 6 | 0 | + 1 | − 13 | − 24 | − 8 | − 7 | − 23 | − 56 | − 16 | − 11 | − 28 | − 84 | − 52 | − 5 | − 78 |
| B | Warp | − 7 | − 9 | − 8 | − 44 | − 18 | − 19 | − 30 | − 63 | − 13 | − 23 | − 37 | − 64 | − 32 | − 37 | − 40 | − 87 |
| | Fill | − 6 | 0 | + 5 | − 29 | − 9 | − 13 | − 11 | − 51 | − 5 | − 10 | − 26 | − 58 | − 32 | − 19 | − 28 | − 86 |
| C | Warp | − 9 | − 6 | 0 | − 33 | − 20 | − 33 | − 46 | − 48 | − 34 | − 39 | − 45 | − 51 | − 45 | − 57 | − 52 | − 81 |
| | Fill | + 3 | − 5 | + 7 | − 7 | 0 | − 13 | − 21 | − 6 | − 24 | − 25 | − 29 | − 17 | − 16 | − 39 | − 28 | − 70 |
| D | Warp | + 2 | + 6 | + 17 | − 1 | − 7 | + 5 | + 9 | 0 | − 18 | 0 | + 5 | − 32 | − 41 | − 34 | − 5 | − 82 |
| | Fill | + 4 | 0 | + 7 | + 2 | − 6 | + 4 | + 9 | − 5 | − 21 | − 16 | 0 | − 17 | − 52 | − 39 | + 6 | − 75 |
| E | Warp | − 12 | − 5 | + 5 | − 18 | − 14 | − 13 | − 17 | − 18 | − 13 | − 16 | − 22 | − 25 | − 41 | − 36 | − 29 | − 59 |
| | Fill | − 4 | − 3 | + 2 | − 3 | − 6 | − 3 | − 4 | + 2 | − 15 | 0 | 0 | − 6 | | | | |
| F | Warp | 0 | + 5 | + 7 | − 6 | − 6 | − 8 | + 1 | − 7 | − 9 | − 8 | − 4 | − 10 | − 12 | − 26 | − 9 | − 40 |
| | Fill | + 6 | + 1 | + 19 | − 5 | + 3 | 0 | + 7 | 0 | + 3 | − 1 | + 12 | 0 | − 2 | − 23 | 0 | − 25 |
| G | Warp | − 3 | − 1 | + 5 | − 9 | − 8 | − 6 | − 13 | − 28 | − 12 | − 7 | − 15 | − 29 | − 39 | − 41 | − 19 | − 80 |
| | Fill | + 10 | + 2 | + 5 | + 6 | − 10 | + 9 | − 3 | − 2 | − 20 | − 10 | − 6 | − 8 | − 54 | − 37 | − 9 | − 75 |

celerating effects of the finish may be noted; *i.e.,* some of the fabrics show greater losses in strength than the grey fabric. It is interesting to note that during long periods of exposure, the unfinished material exhibits better performance at Indio than at any other field location. The better retention of strength by the grey fabric in this exposure in comparison with the other locations was ascribed in part to the absence of mildew and/or acidic fumes (from industrial areas) which may have prevailed at the other locations. During the early periods of exposure, there was usually an increase in strength of the treated fabrics, the greatest increase occurring in the filling direction. This was attributed to a "setting" of the finish which influenced the mechanical properties of the fabric.

The variation in performance of some of the coated fabrics with the location of exposure is emphasized by samples A, D and G. These fabrics exhibited excellent weathering qualities in Washington, while in Indio and New Orleans they were somewhat poorer. The large losses in strength in New Orleans were attributed to the action of mildew, which could readily be observed on the fabrics (see also below). At Indio, however, no mildew appeared to be present, and the inferior performance of A and D at this location is ascribed to a deterioration of the finish, which in turn produced degradation of the cotton duck.

The changes in fire resistance as determined by flame and char during the same periods of exposure are shown in Tables 3 and 4. Three fabrics of the group, A, C and G, exhibited increases in time of flaming during weathering, and it is noted that this change occurred at Indio as well as at the other locations.[5] Since the prevailing conditions were hot and dry, it is apparent that this behavior was not greatly influenced by the extent of rainfall during weathering. The length of char presents a more consistent picture, namely, that all fabrics of this group became deficient in this respect during weathering.

Also of importance is the nature of the degradation of this type of fabric, for a knowledge of this permits a clearer understanding of a means of further improving fabrics for tentage. A number of factors may contribute to the losses in strength of coated fabrics during outdoor exposure. Of greatest interest in this respect are (1) changes in the finish which influence mechanical properties of the fabrics, and (2) degradation of the cotton (a) by the action of acidic degradation products from the finish and (b) by the action of microorganisms. Changes effected by (1) are much less important than changes brought about by (2). In consideration of this particular type of fabric, the action of light on cellulose is precluded since the coating presumably acts as a filter and does not permit the cotton to be exposed to any great quantity of harmful radiation.

[5] The results of one year of exposure at Indio were excluded because of the high sand content of the fabrics. The data were so erratic that no conclusions could be made with respect to fire resistance.

Table 3. Fire Resistance (Time of Flaming) of Duck, Cotton; Fire, Water, Weather, and Mildew Resistant, During Outdoor Exposure for Different Periods of Time at New Orleans (N.O.), La.; Miami (M.), Fla; Washington (W.), D.C. (all beginning in April, 1943); and Camp Young, Indio (I.), Calif. (beginning July, 1943)

| Sample | | Initial | Two Months | | | | Four Months | | | | Six Months | | | | Twelve Months | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | sec. | N.O. sec. | M. sec. | W. sec. | I. sec. | N.O. sec. | M. sec. | W. sec. | I. sec. | N.O. sec. | M. sec. | W. sec. | I. sec. | N.O. sec. | M. sec. | W. sec. |
| A | Warp | 2 | 7 | 6 | 5 | 1 | 23 | 18 | 4 | 6 | 30 | 35 | 17 | 20 | 29 | 25 | 16 |
| | Fill | 1 | 11 | 11 | 2 | 1 | 32 | 13 | 8 | 7 | 31 | 25 | 7 | 19 | 29 | 27 | 20 |
| B | Warp | 1 | 0 | 1 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 5 | 0 |
| | Fill | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 2 | 1 |
| C | Warp | 13 | 4 | 2 | 3 | 1 | 8 | 7 | 3 | 4 | 15 | 8 | 12 | 9 | 26 | 19 | 16 |
| | Fill | 3 | 5 | 3 | 4 | 0 | 15 | 9 | 4 | 5 | 17 | 8 | 5 | 23 | 36 | 18 | 19 |
| D | Warp | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 3 | 2 | 1 | 2 |
| | Fill | 2 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 3 | 1 | 1 | 4 |
| E | Warp | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 6 | 1 | 3 | 2 | 4 | 10 | 13 | 7 |
| | Fill | 1 | 0 | 0 | 1 | 1 | 2 | 1 | 0 | 11 | 1 | 4 | 2 | 6 | 10 | 6 | 7 |
| F | Warp | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 3 | 0 | 2 |
| | Fill | 1 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 2 | 0 | 3 | 0 | 1 |
| G | Warp | 3 | 6 | 23 | 15 | 1 | 20 | 12 | 7 | 38 | 24 | 14 | 28 | 36 | 40 | 24 | 37 |
| | Fill | 1 | 14 | 12 | 10 | 2 | 22 | 19 | 14 | 23 | 32 | 11 | 15 | 39 | 44 | 20 | 38 |

Table 4. Fire Resistance (Length of Char) of Duck, Cotton; Fire, Water, Weather, and Mildew Resistant, During Outdoor Exposure for Different Periods of Time at New Orleans (N.O.), La; Miami (M.), Fla.; Washington (W.), D.C. (all beginning in April, 1943); and Camp Young, Indio (I.), Calif. (beginning July, 1943)

| Sample | | Initial | Two Months | | | | Four Months | | | | Six Months | | | | Twelve Months | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | in. | N.O. in. | M. in. | W. in. | I. in. | N.O. in. | M. in. | W. in. | I. in. | N.O. in. | M. in. | W. in. | I. in. | N.O. in. | M. in. | W. in. |
| A | Warp | 2.2 | 4.1 | 3.9 | 2.8 | 3.9 | 10 | 8.4 | 3.2 | 8.4 | 10 | 10 | 7.5 | 9.0 | 10 | 10 | 8.2 |
| | Fill | 2.1 | 5.6 | 6.8 | 2.4 | 3.5 | 10 | 8.4 | 4.1 | 7.9 | 10 | 10 | 5.1 | 8.5 | 10 | 10 | 10 |
| B | Warp | 1.3 | 1.9 | 2.8 | 1.6 | 2.7 | 10 | 10 | 2.1 | 6.2 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | Fill | 1.4 | 1.9 | 2.7 | 1.7 | 2.4 | 10 | 10 | 2.2 | 3.6 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| C | Warp | 3.2 | 3.7 | 4.3 | 2.9 | 3.4 | 10 | 9.5 | 5.5 | 9.2 | 10 | 10 | 10 | 9.6 | 10 | 10 | 8.8 |
| | Fill | 2.5 | 4.7 | 3.5 | 3.0 | 3.3 | 10 | 7.8 | 4.6 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 9.5 |
| D | Warp | 1.8 | 2.6 | 2.7 | 2.0 | 2.7 | 10 | 5.0 | 2.8 | 4.0 | 10 | 10 | 10 | 3.9 | 10 | 10 | 10 |
| | Fill | 1.8 | 2.5 | 2.7 | 1.9 | 2.2 | 10 | 3.6 | 3.8 | 3.0 | 10 | 10 | 9.5 | 6.2 | 10 | 10 | 10 |
| E | Warp | 1.2 | 2.2 | 1.9 | 1.9 | 2.7 | 2.8 | 2.6 | 2.1 | 7.7 | 3.7 | 4.9 | 3.9 | 7.6 | 7.9 | 7.2 | 8.1 |
| | Fill | 1.2 | 1.9 | 2.9 | 2.6 | 2.7 | 2.7 | 3.2 | 2.1 | 7.7 | 3.6 | 4.9 | 3.8 | 7.6 | 7.7 | 5.4 | 7.4 |
| F | Warp | 1.7 | 3.9 | 2.7 | 3.5 | 2.3 | 9.9 | 8.6 | 2.6 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | Fill | 1.6 | 3.3 | 3.0 | 2.9 | 2.5 | 9.0 | 9.7 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| G | Warp | 2.6 | 4.3 | 6.8 | 5.8 | 2.5 | 10 | 6.1 | 5.0 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | Fill | 1.6 | 5.1 | 6.1 | 4.7 | 3.1 | 9.3 | 6.7 | 6.7 | 10 | 10 | 9.8 | 7.8 | 10 | 10 | 10 | 10 |

Which factor or combination of these factors operates depends upon the type of finish, the weather conditions, etc. Certain facts, which were revealed during the evaluation studies of this group of seven fabrics, may be used to ascertain the nature of the breakdown of duck, cotton; fire, water, weather, and mildew resistant.

It is well recognized that compounds such as chlorinated paraffins, used in this type of fire-resistant fabric, break down under the influence of light, heat, and moisture to produce hydrochloric acid. Thus, in view of the known sensitivity of cellulose to acids, it was first determined whether the presence of acidic substances, either in the finishing material, or resulting from deterioration of the finishing materials, contributed appreciably to the breakdown of the fabrics during exposure in the various field locations. The initial acidity of the fabrics, as measured by the pH of their water extracts indicated the absence of acidic substances in the finishing compounds, the values of the seven fabrics ranging from 7.0 to 9.0. Exposure outdoors led to a lowering of pH, and in the instances of fabrics B and C, the values indicated the presence of acidic substances. (The pH's were, respectively, after 6 months of exposure at Indio, 5.3 and 5.7.) Extensive losses in strength of the remaining fabrics were apparently not accompanied by the formation of excessive amounts of acidic substances.

When the degradation is due to the action of acids, it would be expected that the loss in strength of the fabric would be accompanied by an increase in cuprammonium fluidity, since both of these properties are regarded as functions of the average molecular length of the cellulose chains. (Chapter II, Section B.) Accordingly, the relation between strength and fluidity of the fabrics exposed in the various field locations was determined. The relationships found for the samples after 6 months of outdoor exposure are shown in Table 5. The "theoretical" values listed in this table represent the losses in strength calculated from the fluidity, assuming that the changes in these properties were due completely to acid hydrolysis [6] of the fabric. Similarity between the strength-fluidity relationship of the exposed fabric and the relationship for hydrocellulose may be regarded as evidence of degradation by acid hydrolysis.

In most localities, fabrics B and C exhibited inferior weathering qualities as judged by the loss in both warp and filling strength, and also showed the greatest increase in acidity as measured by "pH." A comparison of the theoretical losses in strength of these samples, calculated from their fluidities, with the losses actually found shows fair agreement,

[6] The basic relation for this calculation was obtained from the strengths and fluidities found for a series of hydrocelluloses prepared by the action of hydrochloric acid on the uncoated fabric (see Figure 4, Chapter II, Section B). In making the comparison of the actual and "theoretical" changes it is assumed that degradation by acidic substances during outdoor exposure is as uniform as the degradation which is produced by the action of a hydrochloric acid solution.

Table 5. Fluidity in Cuprammonium ($F_c$) of Duck, Cotton; Fire, Water, Weather, and Mildew Resistant, After Outdoor Exposure for Six Months at New Orleans, La.; Miami, Fla.; Washington, D.C.; and Indio, Calif.

| Sample | | New Orleans $F_c$ | New Orleans Change in Strength Actual | New Orleans Change in Strength Theoretical | Miami $F_c$ | Miami Change in Strength Actual | Miami Change in Strength Theoretical | Washington $F_c$ | Washington Change in Strength Actual | Washington Change in Strength Theoretical | Indio $F_c$ | Indio Change in Strength Actual | Indio Change in Strength Theoretical |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | rhes | % | % | rhes | % | % | rhes | % | % | rhes | % | % |
| Uncoated | Warp | 8 | − 68 | − 6 | 8 | − 58 | − 6 | 24 | − 55 | − 58 | 13 | − 28 | − 18 |
| | Fill | | − 68 | − 11 | | − 43 | − 11 | | − 49 | − 52 | | − 25 | − 22 |
| A | Warp | 3 | − 40 | − 1 | 4 | − 20 | − 1 | 6 | − 15 | − 3 | 6 | − 48 | − 3 |
| | Fill | | − 56 | − 3 | | − 16 | − 3 | | − 11 | − 7 | | − 28 | − 7 |
| B | Warp | 11 | − 13 | − 13 | 11 | − 23 | − 13 | 15 | − 37 | − 27 | 14 | − 64 | − 23 |
| | Fill | | − 5 | − 17 | | − 10 | − 17 | | − 26 | − 27 | | − 58 | − 25 |
| C | Warp | 12 | − 34 | − 15 | 16 | − 39 | − 32 | 17 | − 45 | − 35 | 9 | − 51 | − 8 |
| | Fill | | − 24 | − 20 | | − 26 | − 31 | | − 29 | − 33 | | − 17 | − 13 |
| D | Warp | 3 | − 18 | − 1 | 3 | 0 | − 0 | 5 | + 5 | − 2 | 6 | − 32 | − 3 |
| | Fill | | − 21 | − 3 | | − 16 | − 2 | | 0 | − 6 | | − 17 | − 7 |
| E | Warp | 7 | − 13 | − 5 | 6 | − 16 | − 3 | 7 | − 22 | − 5 | 6 | − 25 | − 3 |
| | Fill | | − 15 | − 9 | | 0 | − 7 | | 0 | − 9 | | − 6 | − 7 |
| F | Warp | 5 | − 9 | − 2 | 9 | − 8 | − 7 | 8 | − 4 | − 6 | 10 | − 10 | − 10 |
| | Fill | | + 3 | − 6 | | − 1 | − 12 | | + 12 | − 11 | | 0 | − 15 |
| G | Warp | 3 | − 12 | − 1 | 4 | − 7 | − 2 | 6 | − 15 | − 3 | 4 | − 29 | −2 |
| | Fill | | − 20 | − 3 | | − 10 | − 4 | | − 6 | − 7 | | − 8 | − 4 |

Table 6. Changes in Breaking Strength and Fire Resistance of Duck, Cotton; Fire, Water, Weather, and Mildew Resistant, After Exposure for 12 Months in Different Locations (June to December, 1944)

| Sample | | New Orleans Change in Strength % | New Orleans Flame sec. | New Orleans Char in. | Yuma Change in Strength % | Yuma Flame sec. | Yuma Char in. | Washington Change in Strength % |
|---|---|---|---|---|---|---|---|---|
| Uncoated | Warp | − 93 | — | — | − 36 | — | — | − 60 |
| | Fill | — 93 | — | — | − 26 | — | — | − 56 |
| H | Warp | − 42 | 2.6 | 10 | − 52 | 0.2 | 10 | − 21 |
| | Fill | − 28 | 1.6 | 10 | − 37 | 0 | 10 | − 12 |
| I | Warp | − 17 | 0 | 10 | − 50 | 0 | 10 | − 15 |
| | Fill | − 10 | 0 | 10 | − 47 | 0 | 10 | − 7 |
| J | Warp | − 18 | 0 | 10 | − 58 | 0 | 10 | − 14 |
| | Fill | − 18 | 0 | 10 | − 50 | 0 | 10 | − 18 |
| K | Warp | − 11 | 0 | 9.7 | − 50 | 0 | 3.3 | − 15 |
| | Fill | − 13 | 0 | 7.3 | − 57 | 0 | 1.9 | − 11 |
| L* | Warp | − 85 | 0 | 10 | − 15 | 0 | 6.0 | − 9 |
| | Fill | − 95 | 0 | 10 | − 11 | 0 | 4.3 | − 14 |

* Contained pentachlorophenol; used as a control fabric.

point of cuprammonium fluidity than from that of change in breaking strength. Thus, in spite of the apparent accelerating effect of copper naphthenate as judged by the fluidity, the fabrics proofed with this compound exhibit a better retention of strength in areas where microorganisms

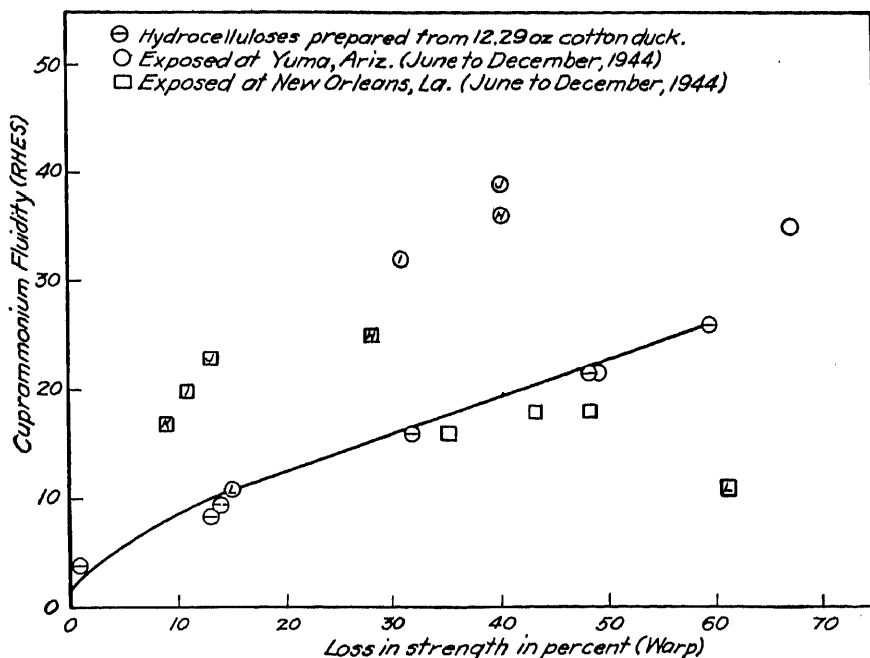



Figure 5. Strength-fluidity relationships of flameproofed tentage fabrics after outdoor exposure.

are active (New Orleans) than fabrics proofed with other types of fungicides.

## B. CAMOUFLAGE NETTING

*P. C. Botzenmayer, Jr.*

### 1. General Requirements

The fundamental requirements of all camouflage materials, *i.e.*, shrimp netting, burlap and Osnaburg garnished fish nets, etc., are to afford complete protection for personnel and equipment from (1) visual observation, (2) infrared photographic observation, (3) fire hazards, etc. A camouflaged installation would not only be worthless from the standpoint of detection but present a serious hazard if the materials used for camouflage, that is, shrimp netting, burlap and Osnaburg garnished fish nets, were in themselves flammable. The presence of such a hazard not only

would endanger the lives of the troops in the immediate vicinity but also in the event of fire would surely attract enemy gunfire. Camouflage shrimp netting, burlap and Osnaburg garnished fish nets, etc., used to conceal gun installations, trucks, planes and field equipment in general are always liable to fire from the flash from a gun barrel, flying pieces of burning powder bags, enemy tracer bullets, or poor camouflage discipline. For these reasons camouflage netting must be flameproofed, or at least highly flame resistant.

Camouflage fabrics must possess several other properties equally as important as flame resistance, such as (1) a treatment permanent enough to retain its effectiveness for at least 6 months under all conditions of outdoor weather, (2) a low add-on, but sufficiently high to afford suitable flame resistance, (3) light-fast colors that possess the required degree of infrared reflectance, (4) mildew resistance, (5) flexibility sufficient to render the fabric useful for camouflage drapes, nets, etc., (6) light weight for ease of handling.

To obtain the above qualifying characteristics for camouflage fabrics, *i.e.*, shrimp netting, burlap and Osnaburg garnished fish nets, work was undertaken at the Engineer Board, Fort Belvoir, Virginia, shortly after the outbreak of the war. The plan of this work was to develop a coating or an impregnation that would, when applied to cotton or jute fabrics, render them flame resistant and also incorporate the other necessary properties previously mentioned.

## 2. Relative Suitability of Treatments

A great many materials which are water-soluble and which can be applied from water solutions are available. In the field of more permanent treatments which do not have to be renewed after each exposure to water or weather, several noteworthy advances have been made in the past few years. A survey of the field of temporary and durable flameproofing processes was presented in Chapter V. The following pages relate the experiences of the Engineer Board in adapting available treatments to camouflage fabrics.

**Water-Soluble Salts.** The first attempts made to obtain the required properties for flame-resistant camouflage fabrics was to coat or impregnate the fabric or netting with water-soluble inorganic salts and by means of a second treatment render the salts insoluble in the fabric fibers themselves. Some of the salts investigated were ammonium phosphate, ammonium sulfamate, sodium silicate and sulfamic acid. The results obtained by this method were by no means suitable for camouflage fabrics that must be weather resistant as well as flame resistant.

**Antimony Oxide-Chlorinated Body Mixtures.** Because of the poor results obtained with the preceding type of treatment, practically all of

the subsequent work was based on the use of material of an organic nature. The adaptation of chlorinated organic compounds for use as basic flameproofing materials represented an important step forward. As was pointed out in Chapter V, certain organic compounds containing chlorine, such as chlorinated paraffin, in combination with antimony oxide and an antiglow agent, produce a basic mixture which with certain additions can be worked into suitable formulations for flame-resistant treatments for fabrics.

Chlorinated paraffins are a series of non-flammable plasticizers and resins produced on a large scale by reacting paraffin wax with chlorine under proper, carefully controlled conditions. The reaction is one of substitution and not addition.

The chlorinated paraffins produced in this manner range from liquids to brittle resins, depending upon the percentage of combined chlorine. Because of this and because of the great number of different types of paraffin wax and other high molecular weight liquid and solid hydrocarbon mixtures derived from petroleum available for chlorination, a large number of chlorinated paraffins can be produced. The term chlorinated paraffin, therefore, does not refer to any one chemical compound or series of chemical compounds but rather to a series of homogeneous mixtures of products with fairly constant and uniform chemical and physical properties.

In this discussion the chlorinated paraffins considered will be limited to those three types which are of greatest commercial interest at the present time. These compounds, which are made by chlorinating paraffin wax having a melting point of about 125° to 130° F., comprise (1) a non-volatile liquid with about 43% combined chlorine, (2) a soft, solid resin with approximately 60% combined chlorine and (3) a hard brittle resin containing about 70% combined chlorine.

Preliminary results indicated that a fairly good flame-resistant treatment for camouflage fabrics having a relatively open weave could be obtained. Camouflage shrimp netting, burlap and Osnaburg garnished fish nets all have a loose and open weave. This fact in itself makes these fabrics more difficult to treat for flame resistance than the regular U. S. Army duck. The open weave makes an abundant supply of oxygen available at the surface of each fiber and as a result combustion can proceed faster and to a greater degree than it can on the closely woven U. S. Army duck.

Formulations containing chlorinated paraffin (42% available chlorine), antimony oxide and an anti-glow agent in combination with coloring pigments, inert pigments, a fungicide and solvents produced an impregnating compound that possessed a promising degree of flame resistance. It was obvious, however, that many corrections would have to be made so that the finished fabric would meet the requirements set forth for a military camouflage fabric. This first treatment containing chlorinated paraffin-

antimony oxide possessed many undesirable characteristics, namely, (1) a persistent afterglow, (2) excessive crocking, (3) loss of breaking strength during heat aging and accelerated weathering exposure tests, (4) loss of breaking strength during storage, (5) poor color durability, and (6) tackiness. In order to overcome the above undesirable qualities, laboratory experiments were undertaken to determine the best combination of materials to produce the most suitable treatment for flame-resistant camouflage fabrics.

**Chlorinated Constituent.** The first selection to be made was to find the best type or grade of chlorinated paraffin. There was a choice of using one of three types or combinations of the three, namely, chlorinated paraffin containing 42%, 60%, or 70% available chlorine. There were other considerations that had to be dealt with: some chlorinated paraffin manufacturers stabilized their product to prevent the formation of free hydrochloric acid; other manufacturers' products contained traces of free iron which would act as a catalyst in freeing hydrochloric acid. In all cases the so-called stabilized grade of chlorinated paraffin was used. Three formulations identical in all details except for the chlorine bearing components were prepared, the first containing the 42% grade of chlorinated paraffin, the second the 60%, and the third the 70% grade. All of these formulations contained the same percentage of available chlorine. The formulation containing the 60% material seemed to be slightly superior to either of the other two. Full pigment value was not obtained using the 42% material and low flexibility was obtained using the 70% grade. Further study showed that a very good combination could be obtained by using a combination of the 42% and 60% grades of stabilized chlorinated paraffin. A combination of 40 parts by weight of the 60% material and 60 parts by weight of the 42% grade gave a basic vehicle having desirable properties. This combination of 42% and 60% chlorinated paraffin when applied to fabric showed some signs of crocking as well as incomplete wetting of the fabric. It appeared from this work that it would be advisable to incorporate a non-oxidizing resin that would have, in effect, three jobs to do, namely, (1) give a better grinding medium which would aid materially in obtaining a better dispersion of the coloring pigments thereby giving full value for each pound used, (2) aid in wetting the fabric, thereby insuring complete impregnation, and (3) reduce the crocking and increase the durability.

**Added Resins.** Since neither urea-formaldehyde nor melamine-formaldehyde type of resin is of the oxidizing type, formulations containing either urea-formaldehyde or melamine-formaldehyde were tested in combination with the 42/60% chlorinated paraffin. The compositions containing the urea or melamine as a part of the vehicle were far superior to compositions that made use of the chlorinated paraffin alone for the vehicle. There was no noticeable difference between the urea or melamine

formaldehyde; both worked very well, and were much better than the alkyd resins that were tested under the same conditions. The wetting of the fabric during impregnation, the resistance to crocking and the durability were all improved by the addition of the resin. Numerous laboratory data have proved that this combination was satisfactory for the intended purpose and superior to most of the formulations tested. These laboratory data include laboratory-prepared samples as well as large-scale commercial production samples.

**Glow Retardant.** The next step in this investigation was to select a material that would reduce the persistent afterglow, which in many cases would consume the entire sample or net. Some of the anti-glow agents studied were ammonium phosphate, the silicates, zinc borate, and melamine pyrophosphate. The melamine pyrophosphate while slightly superior to any of the other materials tested was not available in sufficient quantities to be of value in a program as large as was planned. The second choice was a specially prepared grade of sparingly water-soluble zinc borate which under weak acid or mild alkaline conditions was found to be the best anti-glow agent in combination with chlorinated paraffin and antimony oxide. The zinc borate seems to have at least two desirable effects in a flame-resistant coating or impregnation. First, it reduces afterglow through the liberation of boric acid as discussed in Chapter V, Section B–3–a, and secondly, it appears to accelerate the decomposition of the chlorine bearing materials at combustion temperatures, thereby producing hydrogen chloride gas which acts in conjunction with antimony oxide according to the flameproofing mechanism described in Chapter V.

There is considerable experimental evidence to show that an unstable compound containing hydrogen and chlorine in combination when stored at high temperatures will release more hydrogen chloride when zinc borate is present. This fact clearly indicates that the zinc borate acts as a catalyst at elevated temperatures. This property, when controlled, is very valuable. It may, however, be just as detrimental if used incorrectly. In order to prevent this premature catalytic action and also to neutralize hydrochloric acid that may be formed in the course of use or storage, calcium carbonate is added to many formulations. The use of calcium carbonate in this respect serves two purposes; first, it neutralizes any small amount of hydrochloric acid formed, and, secondly, also acts as a pigment extender in the general formulation.

Antimony oxide was used in all formulations in conjunction with zinc borate, calcium carbonate and chlorinated paraffin. The antimony oxide-chlorinated paraffin combination is of course the basic flameproofing constituent as pointed out in Chapter V. Experimental data show that good flame resistance is obtained when at least 17% of the antimony oxide component is deposited on camouflage shrimp netting, burlap and Osnaburg.

**Color Pigments.** The choice of coloring pigments brings up another

matter of considerable importance. Pigments that will produce the required amount of infrared reflectance are not necessarily the best as far as flame and glow resistance are concerned. Coloring pigments used in these compositions may contribute to the flameproofing mechanisms or they may be more or less passive in nature. Pigments such as chromium oxide and lead chromate must be used in camouflage colors because of the high degree of infrared reflectance and color durability which they possess. In some instances, however, the pigments exert an undesirable influence by means of appreciably increasing the glowing tendency of the fabric. This effect may be overcome to a great extent if the balance of the pigment content, both coloring pigments and the inert pigments, are selected with this in mind. The use of antimony sulphide as a tinting pigment will permit the use of less chromium oxide and lead chromate needed to obtain the correct degree of infrared reflectance thereby reducing those constituents which tend to promote undesirable afterglow.

**Fungicide.** The choice of the best material for obtaining mildew resistance is also very important for several reasons. The fungicide used must protect the cotton or jute from attack by fungi that decompose cellulose. The fungicide must be water insoluble and stable. During the course of this study, it was noted that certain of the fungicides accelerated the decomposition of the chlorinated paraffin thereby releasing free hydrogen chloride which in turn would attack the cellulose and reduce the original breaking strength. Laboratory data gathered during the course of this work clearly indicated that the chlorinated diphenyls used in combination with chlorinated paraffin, antimony oxide, zinc borate, etc., would cause decomposition during heat aging and accelerated weathering exposure tests.

Among the fungicides investigated were di-hydroxy-diphenyl-methane, pyridyl mercuric stearate, salicylanilide, and pentachlorophenol. Of the above fungicides tested, the pyridyl mercuric stearate gave the best results with regards to preventing the growth of fungi on the treated fabric; it had no adverse effect on the balance of the formulation; in fact, it appeared to increase the durability of the treated fabric possibly because it tends to shed water. Pyridyl mercuric stearate has some advantages over most of the other fungicides mentioned above. It can be milled into the composition without any difficulty whatsoever; it is not toxic, and can be handled without causing trouble.

**Add-On.** Since the flame resistance, weathering qualities and other requisites of finished camouflage materials are largely inherent in the impregnant, it is obvious that the quantity of the impregnant applied to the fabric is of primary importance. The most effective formulation will be ineffective if applied in too low proportion to the weight of the unfinished fabric. Forty-five per cent of the dry weight of the unfinished fabric was established as the safe minimum to prevent flaming for com-

pounds containing 17% or more of antimony oxide. If the antimony oxide content of the compound is lower, then the add-on must be increased so that a 17% weight add-on is obtained.

**Formulations Developed.** The following formulations and laboratory test data illustrate some of the advantages and disadvantages pointed out above:

The first two formulations given are typical examples of finishes applied to camouflage shrimp netting that failed to meet the specified requirements as set forth under general requirements.

Formulation A

| Material | % by Weight |
|---|---|
| Chlorinated Paraffin 42% | 29.5 |
| Antimony Oxide | 12.0 |
| Zinc Borate | 18.0 |
| Alkyd Resin | 4.0 |
| Triethanol amine | 0.3 |
| Calcium Carbonate | 2.7 |
| Chromium Oxide Green | 20.0 |
| Iron Oxide (Lemon Yellow) | 4.0 |
| Red Iron Oxide | 1.0 |
| Red Iron Oxide — dark | 1.0 |
| Medium Chrome Yellow | 5.0 |
| Monastral Blue 10% | 2.0 |
| Pentachlorophenol | 0.5 |
| Total | 100.0 |

Camouflage shrimp netting impregnated with the above composition did not produce satisfactory flame resistance. The impregnated netting was tacky; the infrared reflectance was low; the finish "crocked" excessively; and there was an excessive loss of tensile strength after heat aging and accelerated weathering. The color durability was not good; the net "yellowed" during accelerated weathering.

Formulation B

| Material | % by Weight |
|---|---|
| Chlorinated Paraffin 42% | 27.2 |
| Alkyd Resin | 3.0 |
| Aluminum Stearate | 0.3 |
| Calcium Carbonate | 3.0 |
| Asbestine | 1.6 |
| Zinc Borate | 12.0 |
| Antimony Oxide | 9.8 |
| Chromium Oxide Green | 9.3 |
| Lead Chromate | 2.3 |
| Molybdate Orange | 1.0 |
| Thinner (mineral spirits) | 30.0 |
| Pentachlorophenol | 0.5 |
| Total | 100.0 |

Formulation B was better than Formulation A but still far below the standards required. The flame resistance was fair; this could have been improved by replacing the alkyd resin with either melamine-formaldehyde or urea-formaldehyde resin as a part of the binder or film-forming vehicle. The color durability was also better than that of Formulation A, but not good enough to meet the specified requirements.

Samples of camouflage shrimp netting impregnated with Formulation C, made using the 42% grade of chlorinated paraffin for the total amount of available chlorine, have satisfactory properties when the balance of the formulation is well stabilized. As may be noted, this formulation contains a well balanced ratio of antimony oxide, chlorinated paraffin, zinc borate, and calcium carbonate.

Formulation C

| Material | % by Weight |
|---|---|
| Chlorinated Paraffin 42% | 37.4 |
| Pigment D | 17.3 |
| Light Chrome Yellow | 1.5 |
| Antimony Oxide | 13.3 |
| Zinc Borate | 10.7 |
| Calcium Carbonate | 10.2 |
| Aluminum Stearate | 0.5 |
| Asbestine | 0.5 |
| Urea-Formaldehyde | 8.1 |
| Pyridyl Mercuric Stearate | 0.5 |
| Total | 100.0 |

The tensile strength of the fabric was not affected by exposure to 300 hours of accelerated weathering or an accelerated heat test for 5 days at 175° F. The flame resistance of the fabric was within the specified limits both before and after accelerated weathering.

Samples of camouflage shrimp netting treated with a compound similar to Formulation C, with the exception that the zinc borate was omitted, failed to meet the flame resistance requirements. Formulations used by commercial finishers that failed to meet the flame resistance requirements for camouflage shrimp netting were made suitable in some cases by the addition of zinc borate.

Samples of camouflage shrimp netting impregnated with Formulation D, made using the 60% grade of chlorinated paraffin for the total amount of available chlorine, had all of the properties of those treated with the 42% grade of chlorinated paraffin and in addition, more value of the coloring pigment was obtained because the 60% grade of chlorinated paraffin is a much better grinding medium for the pigments used than the 42% material.

Formulation D

| Material | % by Weight |
| --- | --- |
| Chlorinated Paraffin 60% | 29.1 |
| Pigment D | 19.3 |
| Antimony Oxide | 14.3 |
| Zinc Borate | 14.8 |
| Calcium Carbonate | 11.9 |
| Aluminum Stearate | 0.6 |
| Asbestine | 0.6 |
| Urea-Formaldehyde | 8.9 |
| Pyridyl Mercuric Stearate | 0.5 |
| Total | 100.0 |

Samples of camouflage shrimp netting impregnated with Formulation E, made using the 70% grade of chlorinated paraffin for the total amount of available chlorine, had good flame resistance, but the coating was too stiff and could not be used for camouflage drapes, etc. The color durability of the impregnated net was very poor.

Formulation E

| Material | % by Weight |
| --- | --- |
| Chlorinated Paraffin 70% | 26.6 |
| Pigment D | 20.8 |
| Light Chrome Yellow | 1.5 |
| Antimony Oxide | 16.0 |
| Zinc Borate | 12.4 |
| Calcium Carbonate | 12.9 |
| Aluminum Stearate | 0.6 |
| Asbestine | 0.6 |
| Urea-Formaldehyde | 8.1 |
| Pyridyl Mercuric Stearate | 0.5 |
| Total | 100.0 |

Formulations C and D above are examples of the most satisfactory impregnating compounds tested for use on cotton shrimp netting.[9]

## C. LIFE JACKETS

*Robert W. Webster*

### 1. General Requirements

During World War II, the cotton drill cover for kapok life jackets was required to be flameproofed. In addition to imparting fire resistance to

[9] Pigment D used in the preceding formulations is as follows:

| | *Pts.* |
| --- | --- |
| Light Chrome Yellow | 12.6 |
| Dark Chrome Orange | 1.12 |
| Chromium Oxide Green | 9.26 |
| Antimony Sulfide | 3.64 |

the drill, the specified treatment was resistant to weathering incident to shipboard use and appreciably retarded deterioration of the drill due to outdoor weathering. The detail requirements for the treated drill as covered by Navy Department Specification 27D1C are briefly summarized:

*Fire resistance:* No more than 3 seconds afterflame, 180 seconds afterglow and 4-inch char length using the Vertical-Bunsen burner flame test.

*Breaking strength:* Retention of at least 80% of initial strength after subjection to accelerated weathering test (200 hours in National Carbon Co. X–1–A unit).

*Flexibility:* Approximately as flexible as untreated material after accelerated weathering test and after exposure to 158° F. for 72 hours.

*Cold crack:* No crease or crack when folded after 2 hours at – 30° F.

*Crocking:* No more than standard crock sample.

*Tackiness:* No tackiness after subjection to 158° F. for 72 hours or to the accelerated weathering test.

While research was in progress on the flameproofing of kapok, the waterproof kapok pad covers, comprised of a light-weight polyvinyl chloride resin-coated sheeting, were treated and specially compounded for fire resistance to afford some protection to the kapok.

## 2. Relative Suitability of Treatments

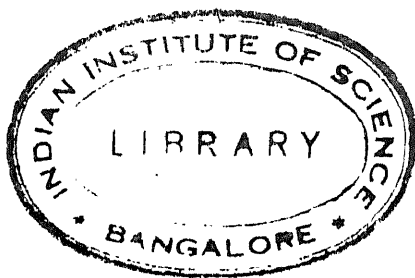
With the participation of this country in World War II, it became imperative that kapok life preservers be rendered fire resistant throughout. Most treatments available at that time utilized water-soluble compounds and were, therefore, unsuitable for life preservers which are worn under all weather conditions. As an expedient, the weather-resistant treatment commonly applied to canvas was accommodated to the lighter cotton drill life jacket cover. Although affording adequate fire and weather resistance this treatment, being of the chlorinated paraffin-antimony oxide type, has the distinct disadvantages of being slightly tacky, of crocking excessively (in spite of efforts to control these properties) and of lacking fastness to laundering. Consequently, research was initiated for the development of a more suitable fire-resistant treatment for the jacket cover. The unavailability of suitable treatments for kapok also made it necessary to initiate laboratory investigation along these lines.

### a. Development of Cover Treatment

An answer to the desire for a treatment eliminating the deficiencies mentioned above is a resin-coated, pretreated drill. Prior to coating on one side with a polyvinyl chloride compound, the drill is impregnated with the well-known chlorinated paraffin-antimony oxide formulation. In this manner a fire- and weather-resistant finish is obtained which is read-

ily cleaned, since the coated side becomes the outer surface, and eliminates the tack and crocking of the former treatment. The results of extensive service tests on life jackets made of this fabric indicate that it has satisfactory serviceability except that the tear strength is apparently insufficient. Current laboratory work is proceeding with a view to improving the tear strength of this coated fabric. In addition, investigations are in progress with the aim of developing a readily cleanable treated fabric utilizing finishes similar to the polyvinyl chloride-antimony oxide treatment. This is intended to eliminate the disadvantages of a coating, *i.e.*, impairment of ventilation which is particularly important when the kapok becomes soaked.

### b. Development of Kapok Treatment

Considerable difficulty was experienced in developing a fire-retardant treatment for kapok which did not deplete its buoyancy to an intolerable degree. Many formulations were submitted which appeared to impart satisfactory fire resistance but reduced the buoyancy to as much as 10% of that which might be expected of untreated Prime Java kapok. A synthetic resin formulation was found which did not impair the buoyancy and which appeared to render the kapok satisfactorily fire resistant. However, full-scale fire tests on life jackets utilizing this treatment proved it to be inadequate as a fire retardant, particularly when the kapok was in a dispersed state. Recently, applications of a powdered inorganic compound have resulted in a treatment quite superior to those previously investigated. With the depletion of stocks of buoyant vegetable fibers and in view of the recent development of an inherently fire-resistant, synthetic, buoyant fiber, such a treatment is not a pressing need at this time.

# Chapter VIII

## Applications to Civilian Fabrics

*J. Labarthe, Jr.*

The writer will never forget a dramatic clothing ignition accident he witnessed in a theater lobby about twenty years ago. A young woman wearing a filmy net evening gown accidentally backed into a lighted cigarette. The dress instantly burst into a flame that billowed high above the victim's head. Several men in the party pulled off their coats and in a matter of seconds smothered the flames and saved her life. Nevertheless, she was terribly burned about the back and head and spent many agonized weeks in a hospital.

Flameproofing of textiles for civilian use received great impetus in 1945 as a result of several fatalities from fires occurring with rayon pile fabrics used in children's clothing. Three boys were fatally burned in Washington, D. C., when cowboy chaps made of long piled rayon became ignited. Several others were seriously injured from the burning of the same type of play clothes. These accidents and others directly attributable to certain types of construction in cotton and rayon fabrics have led to legislative action.[1] It must be kept in mind that consumers' goods include the fabrics and decorations used in places of public assembly as well as the household fabrics, work clothes and other wearing apparel. Thus the terrible Boston Cocoanut Grove night club fire of November 28, 1942, is one more evidence of the tragic results from inadequate flameproofing of consumer goods.

**Statistics of Fire Losses.** According to the Handbook of Fire Protection,[2] the annual direct fire loss in the United States amounted to $319,445,700 per year for the period 1930–1939, inclusive. Unfortunately, the extent to which the loss was due directly to textile flammability cannot be estimated but the effective and easily applied flame-deterrent finishes developed during the war may be expected to result in great savings in life and property.

That Handbook[3] lists the more common causes of loss of life resulting

[1] H.R. 2496. Pending federal legislation, House of Representatives.

[2] Crosby, E. U., Fiske, H. A., and Forster, H. W., "Handbook of Fire Protection," National Fire Protection Association (1941), p. 1.

[3] *Ibid.*, p. 9.

from fires based on typical but not complete records received by the N.F.P.A. Department of Fire Record from June, 1930, to March, 1940. The original causes of fire are not identified, but the lives of 12,837 persons were lost in accidents indicated in the table. The following excerpt lists those incidents which might be partially or wholly attributable to fabric flammability.

Causes of Loss of Life by Fire

| Cause of Loss of Life | Men | Women | Children | Total |
|---|---|---|---|---|
| Children Alone in House | 0 | 0 | 363 | 363 |
| Children Playing with Matches | 0 | 0 | 233 | 233 |
| Clothing Ignited | | | | |
| 1. Bonfires, Burning Rubbish, etc. | 51 | 22 | 98 | 171 |
| 2. Candles and Torches | 5 | 8 | 8 | 21 |
| 3. Electrical Appliances | 13 | 16 | 17 | 46 |
| 4. Fireplaces and Open Grates | 10 | 37 | 23 | 70 |
| 5. Furnaces, Stoves, and Heaters | 49 | 239 | 89 | 377 |
| 6. Smoking and Matches | 60 | 42 | 0 | 102 |
| 7. Smoking in Bed | 158 | 53 | 1 | 212 |
| 8. Miscellaneous | 49 | 53 | 29 | 131 |
| Flammable Liquids and Vapors | | | | |
| 1. Alcohol | 40 | 7 | 5 | 52 |
| 2. Gasoline and Similar Liquids | | | | |
| (*a*) Stoves, Lamps, and Torches | 37 | 43 | 61 | 141 |
| (*b*) Used for Cleaning Purposes | 70 | 125 | 35 | 230 |
| (*c*) Used to Kindle Fire | 44 | 43 | 62 | 149 |
| (*d*) Miscellaneous | 185 | 50 | 86 | 321 |
| 3. Kerosene, Range Oil, and Fuel Oil | | | | |
| (*a*) Stoves, Lamps, and Torches | 78 | 112 | 90 | 280 |
| (*b*) Used to Kindle Fire | 110 | 191 | 228 | 529 |
| (*c*) Oil Furnaces | 5 | 4 | 5 | 14 |
| 4. Paint, Varnish, Removers, Thinners, etc. | 9 | 2 | 2 | 13 |

Decorations in places of public assembly are other kinds of consumer goods that have played a prominent part in several spectacular and tragic conflagrations. Those theater, dance hall, night club, and circus fires resulting in many deaths generally owe such loss of life to a combination of factors including inadequate exits, overcrowded space, flammable decorations, and panic. Official records of four of these fires show that flammable decorations played a prominent part in the resultant loss of life. Probably better selection and more adequate flameproofing of the decorations would have slowed down the rapidity with which the fire spread and thus reduced the loss of life.

**The Study Club Fire.** The Study Club fire[4] in Detroit early in the morning of September 20, 1929, which killed 22 persons and injured 45, was believed to have been caused by the careless dropping of a lighted

[4] *N.F.P.A. Quarterly*, Vol. 23, No. 2, pp. 115–125.

match. Forced ventilation spread the flames with incredible speed through the highly flammable cloth draperies and wax- or lacquer-coated oak leaves hanging from the wooden latticed ceiling.

**A New York Restaurant Fire.** On the evening of February 12, 1936, six men and three women were killed and 34 other persons injured at a church society banquet in Lum's Chinese Restaurant,[5] New York, where fire broke out and panic ensued. The fire originated in the draperies of a men's furnishings store located on the first floor. Attempts to quench the fire with a pail of water were unsuccessful and an open door rapidly spread the flames up the front of the building and, when the window of the second floor restaurant broke from the heat, the draperies and hangings were ignited and the interior was swept by flames.

**The Natchez Dance Hall Fire.** Two hundred and seven negroes died in a Natchez, Mississippi, dance hall[6] on April 23, 1939. The hazards contributing to the death toll of 207 of an estimated attendance of 746 included (1) highly combustible decorations, (2) inadequate exits, and (3) overcrowded conditions. The long, narrow building was of corrugated metal and had once been a garage. The decorations were tinder-dry Spanish moss hanging to a thickness of 6 to 12 inches from wires strung in a criss-cross fashion so as to conceal the ceiling and to give a cave-like appearance to the hall. The moss had hung there for 2 or 3 years and was not flameproofed in any way. The fire started from a cigarette or a match and spread with explosive violence. The flaming decorations fell on the crowd and ignited the clothing of the victims. The building was a veritable corrugated-iron oven and the victims were suffocated and burned by the terrific heat.

**The Cocoanut Grove Night Club Fire.** Boston was the scene of the terrible Cocoanut Grove Night Club fire[7] on the the night of November 28, 1942. The death toll of 489 persons and the heavy toll of injuries marked this fire as one of the worst in our history. The highly flammable cloth-covered ceilings, artificial cocoanut palms, and other decorations contributed greatly to the speed with which the fire spread in a flashing sheet just below the ceiling. Some of the decorations were said to have been flameproofed, but the treatment was apparently inadequate. Burns and lung injuries from the effects of heat and fumes caused some of the injured to die sometime after the fire. The prevalence of lung injuries leads to numerous theories as to the causes. The effect of intense heat on the lung tissue, carbon monoxide poisoning, and nitrous fumes produced by the combustion of pyroxylin-coated textiles are among the explanations advanced to account for the prevalence of lung injury. The actual origin and nature of the fumes have not been identified.

[5] *N.F.P.A. Quarterly,* Vol. 29, No. 4, pp. 318–321.
[6] *N.F.P.A. Quarterly,* Vol. 34, No. 1, pp. 70–75.
[7] *N.F.P.A. Report* (Jan. 11, 1943).

**Furniture and Household Fabrics Damage.** Superficial damage to household fabrics, such as upholstery for furniture, rugs, bedding and the like, is a significant expense to the home owner and to hotels, theaters, and other public and private institutions. Statistics are lacking but no doubt the loss could be greatly reduced if flameproofing treatments were more generally used.

The possible extent of damage that may result from this type of fire is demonstrated in a short news story about a narrow escape of members of the Covington, Kentucky, fire department.[8] A cigarette dropped in an overstuffed couch, smoldered unnoticed and finally resulted in a fire which spread throughout the theater with an estimated loss of $75,000. The collapse of the roof almost trapped nine of the firemen. There is no doubt that this accident is rather typical of those happening daily where a smoldering spark or cigarette encounters a flammable material.

**Flameproofing Treatments.** The mechanism of flame propagation in cotton fabrics and the recent developments in the flameproofing of textile materials have been discussed in the earlier chapters.

From the consumers' standpoint, the primary objective is to reduce or to prevent entirely the type of combustion characterized by flaming. Fatalities and serious personal injuries as well as most property damage result from this class of combustion. The textile product itself may be ruined by the flameless or glowing type of combustion, but fatal accidents and extensive property damage rarely result from this type unless some other, more highly flammable substance is ignited by the glow. Cellulosic fibers flame readily. Some of the flame-preventive treatments thus far available to the public have satisfactorily controlled flammability under certain circumstances, but the so-called "afterglow" may continue after the source of flame has been removed. In clothing fabrics this afterglow may attain temperatures higher than the flame and may produce serious burns before the garment can be removed. Doubtless the terminology must be clarified to avoid misunderstanding among manufacturers, processors, retailers, and consumers. Textiles that are readily flammable should positively not be used for wearing apparel nor for decorative purposes in any place of public gathering. Non-flammable or flameproofed fabrics may char and, in fact, may be weakened and made useless by heat, but they should not readily support combustion when in contact with a lighted match or a glowing cigarette. These fabrics are not fireproof in the sense that asbestos fiber fabrics and fiber-glass fabrics will not burn.

Recognizing that positive steps could be taken against accidental fires, the U. S. Department of Agriculture issued a pertinent booklet, "Fireproofing Fabrics,"[9] in 1937. The purpose was to disseminate information

[8] *Volunteer Firemen,* 12, p. 23 (1945).

[9] "Fireproofing Fabrics," Farmers' Bulletin No. 1786, U. S. Dept. of Agriculture; revised 1938.

on the fireproofing of children's clothes, curtains, draperies, and other flammable household fabrics so as to reduce the incidence of farm fires that have been estimated to take more than 3500 human lives each year.[10]

The extent to which the suggested borax-boric acid treatment methods have been utilized is not known; it is reasonable to assume, however, that household textile products exposed to particularly serious fire hazards in farm and rural communities lacking mechanized fire-fighting equipment have been treated rather extensively. Teachers of home economics and county demonstration agents have stated that many farm families do flameproof kitchen curtains, aprons, ironing board covers, pot holders, and cotton rugs and fabrics placed near coal stoves or open fireplaces.

Municipal fire departments should check on the use of flammable decorations and determine the degree of effectiveness of flameproofing treatments. In many cities ordinances require not only that theatrical scenery and dance hall decorations must be flameproof, but that restaurant, exhibition hall, and even holiday decorations in stores should be protected.

The National Board of Fire Underwriters has issued a booklet titled "An Ordinance Providing for Safety to Life in Places of Assembly."[11] So important does this organization believe decorative materials to be, that they are dealt with in section 2, immediately following the section dealing with the application.

"2. *Decorative Materials.*

"(a) All combustible decorative material, including curtains, acoustical materials, streamers, cloth, cotton batting, straw, vines, leaves, trees and moss, but not including floor coverings, shall be rendered flameproof; provided this shall not be required of materials not exceeding one-sixteenth inch in thickness applied directly to and adhering to a noncombustible base. Such flameproofing, unless certified by Underwriters' Laboratories, Inc., or other laboratories of recognized standing, as being of a permanent nature, shall be tested by the fire department each six months and the treatment renewed if necessary.

"(b) The use of imitation leather (or other material) consisting of or coated with a pyroxylin base is prohibited."

It is significant that in this ordinance "place of assembly" is defined as a "room or space in which provision is made for the seating of 100 or more persons for religious, recreational, educational, political, social, or amusement purposes or for the consumption of food or drink." The permit shall be granted for one year from date of issue and shall be revokable for cause.

**Legislative Action.** Legislative action about fabric flammability, especially of wearing apparel, is not new. In England, sparks from open grates had long been a source of serious fires in homes and some children

[10] *Ibid.*, p. 1.

[11] National Board of Fire Underwriters, Committee on Fire Prevention and Engineering Standards, Suggested Ordinance (Jan., 1943).

had been burned to death where cotton flannel sleeping garments became ignited. A symposium on the flammability and flameproofing of fabrics was sponsored by the British delegates to the Eighth International Congress of Applied Chemistry at its meeting in New York in 1912. The Fabrics (Misdescription) Act was passed in England, August 15, 1913, making it "unlawful . . . to sell or have in possession for sale any textile fabric either in the piecé, or made into garments . . . to which is attributed expressly or inferentially the quality of non-inflammability or safety from fire . . . unless such textile fabric conforms to such standard of non-inflammability as may be prescribed by regulations to be made by the Secretary of State. . . ." The method of test was specified in the Home Secretary's regulation dated January 2, 1914.

Obviously, the English Act places the responsibility in regard to flammability of a fabric on the first party selling it or having it in possession for sale, namely, the manufacturer of the cloth.

In 1945, the California Legislature passed a bill governing the sale of flammable or explosive fabrics. This most recent legislative action in the United States originally pointed toward articles made of nitrocellulose and nitrocellulose-treated fabrics and may be the pattern for other legislation on fabric flammability.

The original bill passed by the California Legislature on January 27, 1945, read as follows: "It is unlawful to manufacture, sell or offer for sale any article of wearing apparel, cloth, drapery, or other fabric or material made from or containing any synthetic fiber which is wholly or in part made from or contains any hazardous explosive or other substance in sufficient quantity so as to make such fabric or material more highly flammable than cotton cloth in its natural state." The law then went on to include miscellaneous items such as "any toy, tool, or other article designed for use or intended to be used in any household or place of abode, containing such hazardous or highly flammable substance." Bonnet[12] has pointed out that "making the flammability depend upon a comparison with cotton in its natural state left the interpretation as to what fabrics are to be considered flammable vague and uncertain, and the law unenforceable."

Mr. J. T. Yockers, California State Fire Marshal, tentatively offered a more practical amendment on March 6, 1946, proposing that:

"The sale in that state of a garment containing any cellulose nitrate product, or containing a fabric that will flash at 400° F. under specified test conditions, would be unlawful."

The amendment included wearing apparel composed of pile or brushed surface fabrics unless the textiles were effectively flameproofed; cellulose nitrate or celluloid buttons, ornaments, and toys; and stuffed toys.

[12] Bonnet, F., "Flammability of Consumer Textiles," Papers of the American Association of Textile Technologists, 1, 50–56 (1945).

This suggested revision obviously points to celluloid and cellulose nitrate materials, articles, and finishes rather than to synthetic fibers. However, some of the synthetic fabrics of hazardous nature were included and a method of test was suggested. Recognizing that numerous articles of regular commerce, such as combs, decorative buttons, celluloid toys for children and even infants' rattles, and pyroxylin-covered fabrics, were specifically referred to, the California Retailers Association sponsored further amendments designed to eliminate all reference to celluloid and cellulose nitrate and in this way placed the onus of fabric flammability on synthetic fibers. Unfortunately, to most persons, the inference is that rayon is by its very nature always a fire hazard, which is certainly not the case.

The California Assembly Bill No. 726, passed April 18, 1945, refers to flammability of merchandise as follows:

"(c) "Inflammable article" as used in this chapter is any article made from or containing natural or synthetic fiber and determined by the Fire Marshal to be so highly inflammable as to constitute a dangerous risk of fire and hazard of injury to persons and property, taking into consideration the use or uses for which the article is made and designed to serve.

"(d) It has recently come to notice that of the various natural or synthetic fibers adapted and adaptable for use in the making of articles, as herein defined, some are so inflammable as to constitute a dangerous risk of fire and hazard of injury to persons and property. Provisions should be made for the avoidance of such risks and hazards by preventing the use of such highly inflammable fibers. It is not feasible by statute to prescribe more specific tests than those herein prescribed, for it would appear that none such have yet been fully developed. It is necessary, therefore, to commit to the State Fire Marshal the conduct of research in these matters, the development of tests for these materials, and the administration of the provisions of this chapter for the prevention of the risks and the avoidance of the hazards described."

The law makes the following statement of the facts to emphasize the necessity for the safety measure:

"It has been ascertained that a few types of articles are of a highly inflammable nature. Most California manufacturers and sellers of articles have not the facilities to determine whether such articles are highly inflammable, and the result of such uncertainty is that in some instances highly inflammable articles will remain where they are dangerous to life and property while in other instances manufacture or sale of useful and safe articles will be discontinued by California firms and may even be destroyed. It is necessary that the State Fire Marshal immediately be given the regulatory powers granted by this act in order that he may prescribe general and uniform regulations which will reduce the risk of fire and hazard of injury to persons and property and at the same time

prevent serious and unnecessary economic injury to many California citizens."

A very similar bill (H.R. 2496) was introduced before the House of Representatives on March 6, 1945. The bill was referred to the Committee on Interstate and Foreign Commerce. It is intended to bar from interstate commerce any fabric "made from or containing any synthetic fiber which is either wholly or in part made from or contains any hazardous explosive or other substance in sufficient quantity so as to make such fabric or material more highly inflammable than cotton cloth in its natural state."

These legislative actions are designed to protect the public but it is immediately apparent that if the public is to be served to its best interests both as to safety and economy, the textile industry must present strong evidence of weaknesses or errors in proposed bills and of its willingness and ability to produce "safe" fabrics in accordance with reasonable legislation. It is obvious that H.R. 2496 implies that the synthetics and particularly rayon are especially dangerous. The fact that brushed rayons, extremely sheer rayons, rayon fabrics with a high pile and some coated fabrics are very flammable may support this implication. But these constructions present a flammable substance, cellulose, in such a condition that there is the maximum of surface area exposed to the air and the least opportunity for free circulation of the air trapped in the depths of the maze of fine filaments and thus the conditions for almost instantaneous ignition are ideal. If any other cellulosic fibers were similarly constructed, the fire hazard would be equivalent to that of rayon. Just what is meant by the prescribed gage of performance is not clear; the "natural state" of cotton cloth is decidedly variable.

The National Retail Dry Goods Association requested the American Association of Textile Chemists and Colorists to investigate test methods and to devise a procedure for the evaluation of the flammability of various constructions of cotton cloths and those from other textile fibers.

**A.A.T.C.C. Test Method for Flammability of Textiles.** Reference has been made to the need for a reproducible test method in order to arrive at a sensible basis on which to rate textiles for flammability hazard and to classify them for conformance to or violation of legislative action. The special committee of the American Association of Textile Chemists and Colorists reported to the members of the organization on January 5, 1946, the tentative test method described in Chapter IV, Section B–2.

It must always be kept in mind that no method of appraisal is a satisfactory test unless it gives reproducible results with each of a wide range of test samples and, further, that statistically valid correlation is achieved by different persons using the method, appliance, or tool within one laboratory and by laboratories in different localities.

Tests with the completed apparatus by the proposed tentative test method led to the following conclusions:

1. Wool, silk, nylon, Vinyon, and Velon fabrics offer no flammability hazard.

2. Cotton is just as flammable as regenerated-type rayon under identical construction and testing conditions.

3. With cotton having a normal moisture content of 6.5%, as compared to regenerated type rayon with 11%, it is reasonable to conclude that cotton will come to the critical point much more rapidly than rayon.

4. If the samples of any one fabric are all in identical condition as to moisture content and physical condition of the face being tested, very close correlation of results within one laboratory and in any other laboratory can be arrived at.

5. Certain coated fabrics, although generally slow to ignite, burn with a violent flame which is difficult to extinguish and therefore offer a very definite hazard.

A number of samples, none of which were flameproofed, were tested on this apparatus with the following results:

1. All rayon fluff knit—low brushed Bemberg face: burned only in a slight circle.

2. White cotton flannelette—low brushed face: burned only in a slight circle.

3. Viscose rayon twill—medium low pile face: burned at times varying from 10 to 23 seconds.

4. Viscose rayon medium pile fabric—dense face length of pile approximately 3/32-inch: burned in 9.5 seconds.

5. Viscose rayon netting: burned rapidly with complete combustion in 5 to 6 seconds.

6. Acetate rayon netting: burned in 5 seconds with a very slight volume of flame, but melted during combustion, and drops of burning molten material dropped through the grid.

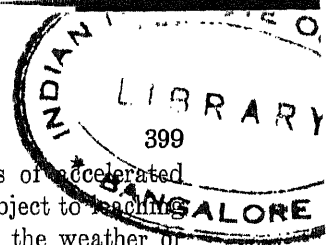
7. Cotton blanket fabric: burned in 10 seconds.

8. Cotton warp, 50% cotton, 25% wool and 25% rayon face blanket fabric: burned in 14.2 seconds.

9. Long-pile viscose face rayon fabric: burned in 5 to 6 seconds.

10. Pyroxylin-coated fabric: did not ignite on the first application of the flame; did ignite on the second application to the same point and burned with a very intense large volume flame.

**Recommended Requirements.** Recommended requirements for flameproofing of textiles must necessarily be based upon a standard method of evaluation. In 1938, the National Fire Protection Association recommended a series of requirements for textiles intended for different uses. These suggestions were adopted by the N.F.P.A. Committee on Fireproofing and Preservative Treatments and adopted by the Association in 1940–1941.[13] The committee recommended test methods by which interior deco-

[13] "Recommended Requirements for Flameproofing of Textiles," National Fire Protection Association, International 1941 (reprint 1945).

rative materials should be evaluated and also methods of accelerated weathering and flameproofing testing for those fabrics subject to leaching with water from such causes as laundering, exposure to the weather or hose streams.

The appendix lists a number of other standard test methods, details of which have been given in Chapter IV, Section B–2.

The National Board of Fire Underwriters [14] points out that in making flameproofing tests "it apparently makes little difference if the testing flame is a match, candle or blow torch since actual ignition is largely a matter of supplying a sufficient quantity of heat to raise a portion of the material to the ignition temperature." This comment refers to field test appraisals of decorative materials and should be distinguished from the more precise laboratory test methods. The field test is simply intended to determine whether the textile product contributes to the spread of the flame after the source of ignition has been removed and is commonly used to measure the permanence of the finish during use. Laboratory appraisals are for research and control purposes, to serve as bases for purchase, and to measure conformance to legal requirements.

**Implied Warranty.** On July 5, 1945, the U. S. Circuit Court of Appeals of the District of Columbia reversed the decision of the District Court in favor of a department store by ruling that it was the responsibility of the store to see that a chenille lounging robe was "reasonably fit for use as a robe." The case involved a suit by a customer for $50,000 as alleged damages resulting from burns. The customer accidentally ignited the robe by waving a match after lighting a cigarette, and the flame spread over the robe with great speed.

Lawsuits totalling more than $800,000 were brought against another Washington store by the parents of the three boys burned to death when their brushed rayon cowboy chaps were ignited.

Thus, whenever it can be established that a fatal accident has been caused by the combustion of a flammable fabric, to the sorrow and economic strains imposed on the family of the victim must be added the possible economic loss to the distributor, garment manufacturer, and textile producer. It has been mentioned previously that according to the English Fabric Misrepresentation Act, the ultimate responsibility rests with the textile producer. If implied warranty of complete safety from fire is applied to all textile outerwear regardless of the fiber and the fabric construction, department stores should demand that flammable fabrics be given a flameproofing treatment. Garment manufacturers likewise may demand this flameproof protection of their fabrics, as the responsibility for fatal accidents may be passed on to them by the distributors.

The opinions of department store buyers are sharply divided on the degree of the peril of fabric flammability and many of them seem to have

[14] National Board of Fire Underwriters, Special Interest Bulletin, No. 213 (Apr. 16, 1945).

overlooked this potential danger in numerous items of their stock. Undoubtedly the threat of "implied warranty" is not generally recognized and considered.

A brief survey was made of the opinions of textile products buyers in a large department store. Three simple questions were asked:

1. What textile items in your stock would have additional protective value and sales appeal if they were flame resistant?

2. If they were flame resistant and there were no adverse qualities imparted to the goods, such as skin irritation, poor hand, increased stiffness, etc., would the treatment be worth a slight extra charge? If so, how much more do you think your customer would be willing to pay for this added safety?

3. Do you think that a flame-resistant finish would give you a worthwhile sales point that you could advertise to advantage?

A few typical replies show that the problem of potential fire hazard in textile and plastic merchandise is not fully realized.

A buyer in toys reported, ". . . the only item in the toy department that should and could be flameproof is playsuits for children . . . would be an advertising feature and a slight additional cost for this treatment would be in line." The flammability of untreated plush toys and of celluloid products was not considered to be important, to mention only a few other items that do not mix well with matches and open fires.

A buyer of robes and lingerie recommended that "rayon suede robes and chenille robes should be flameproofed . . . probably 50 cents to a dollar might be a reasonable charge . . . would be a real sales point . . . and robes with long sleeves are very dangerous around the kitchen or in firing the furnace."

A buyer in home furnishings was of the opinion that "the process might be advantageous in curtains, draperies, blankets, and slip covers . . . not worth a premium . . . and very little advertising value."

A buyer of children's clothing advised flameproofing for a wide variety of children's and infants' outerwear and coverings commonly made of brushed or napped rayon or cotton, and added, "I think a dollar should be the maximum extra charge; however we should know the permanence of the finish in use and cleaning and how costly a re-finish would be . . . a real advertising sales point." Another buyer in a similar department believed no treatment was called for.

A work clothing department head recommended, "coveralls or overalls should be flameproofed, especially those used by painters, bricklayers, carpenters, and other workmen engaged in outside jobs using torches. It would be a good selling point and possibly a dollar more for the garment."

A buyer of girls' clothing urged that "flammable robes, sleeping garments, snowsuits, skating costumes and Girl Scouts' camp items should be treated . . . the cost to be absorbed in the retail price . . . such treat-

ment would be advantageous for use in advertising *if children do not become experimental.*" Following this line of thought, another buyer believed that the presence of flameproofing should not be advertised "because it might induce experimental curiosity."

The survey showed the opinion to be equally divided as to whether an extra charge would be warranted. It was interesting to note that for furniture and upholstery the buyers believed that a treatment would be of value only if it prevented charring and marking from cigarettes and matches. Reduced fire hazard was judged to be more important commercially than in the private home.

The additional personal and property safety resulting from flameproofing many common textile products carried in their stock was overlooked by several buyers. For example, no mention was made of party costumes, play tents, camping tents, pot holders, ironing board covers, bathroom curtains, shower curtains, garment bags, bridge table covers, ski togs and winter sport clothes in general, table linens, aprons, coated fabrics and numerous other items.

The flameproofing treatments of consumer goods fall into two categories, namely, the permanent treatments that will not lose effectiveness during use, exposure, or cleaning, and those that must be renewed after each cleaning, washing, or exposure to rain. Labels must identify the type and durability of the finish on the goods so that the garment or textile product manufacturer, the retailer and the customer will utilize the flameproofed fabric to the best advantage and in the proper end-use application. There is danger of a sense of false security if the very flammable fabric weaves are not permanently protected upon reaching the ultimate consumer.

**Research Program Indicated.** In spite of the greatly improved flameproof finishes developed for use in war, the suitability of these agents for civilian goods and the development of still better finishes and processes can only be established by intensive research.

Technical investigation must determine

1. the most effective permanent and easily renewable flameproof treatments for cellulosic fibers;

2. the most effective permanent flameproof treatments for pyroxylin-coated fabrics;

3. the production of finishes or the perfection of processing to provide finishes that will be harmless to infants who may chew the cloth, non-irritating to the skin, and non-harmful to the fabric strength, color, or texture;

4. simple and effective methods for re-application of finishes in the home;

5. the adequacy of the A.A.T.C.C. or an improved standard testing appliance lest the lack of a dependable method of fabric flammability

evaluation, result in discriminatory control legislation and local ordinances.

In addition to the technical research program, a well-planned and well-conducted educational program must be carried out. No one will argue against the fact that some fabrics on the market are dangerously flammable and must be flameproofed or removed from certain end-use applications. Nevertheless, it must be recognized that rayon fibers are no more flammable than cotton fibers in the same fabric construction and a poorly planned campaign conducted in the public safety might create false fears and prejudices. It is probable that many department store buyers are uninformed as to the advantages of flameproofing and as to their responsibility to the public safety and to the possible legal actions against the stores in the occurrence of fatal accidents or serious injuries resulting from fire. Garment manufacturers and other producers of consumer goods and the retail distributors of these products should be the first groups exposed to the educational program.

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